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Stable isotopes of bioelements for tracing limnological key processes in the Osterseen lake district, Upper Bavaria

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STABLE ISOTOPES OF BIOELEMENTS FOR TRACING
LIMNOLOGICAL KEY PROCESSES IN THE OSTERSEEN LAKE
DISTRICT, UPPER BAVARIA



EMANUEL LEANDER BRAIG

Summary

The significance of stable isotopes of the bioelements for the investigation of hydrological as well as carbon and nitrogen cycling processes has been shown in many ecological studies. Key insights into the water cycle have been gained by the use of stable isotopes of hydrogen and oxygen as naturally occurring tracers, while carbon and nitrogen stable isotopes of sedimented organic matter (SOM) have successfully been utilized as proxies e.g. for paleoproductivity.

However, in particular for stable isotope research in lacustrine environments several key aspects have not yet been explored in sufficient detail. The suitability of oxygen stable isotopes for tracing of hydrological key processes such as entrainment of hypolimnetic waters during stagnation or annual turnover have not been assessed over a broad range of lacustrine mixing types. As well, the widespread use of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) stable isotope ratios for trophic history reconstruction frequently rests upon the assumption that primary productivity provides the dominant input fraction of SOM and that its signal remains largely unaffected by pre- and postburial alteration. But that hypothesis has been challenged by the results of recent investigations, which ascribed the primary control of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM to the extent of anoxia in the water column and sediment and the associated microbial reworking before and after sedimentation.

Therefore, the first primary objective of the present thesis was to test the suitability of oxygen stable isotope ratios ($\delta^{18}\text{O}$) for tracing limnological key processes and to collect qualitative information on the reaction of the signal to several limnological phenomena present in the Osterseen lake district, such as polymixis in Waschsee, meromixis in Eishaussee and subsurface groundwater inflow in Fohnsee.

The second primary objective was to test a conceptual model ascribing the control of the SOM carbon stable isotope signal not only to epilimnetic primary productivity but to anaerobic methanogenetic processes in a case study at Fischkaltersee. As well, the effect of different mixing types and bottom water oxygenation conditions on the conservation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signals in SOM was explored in Eishaussee. As a secondary objective, it was tested whether the trophic development of the lakes was reflected in sedimentary proxies by comparing their records with existing data on the eutrophication history.

In order to address the first objective, water sampling and depth profile measurements of various physical parameters (water conductivity ($\mu\text{S cm}^{-1}$), temperature ($^{\circ}\text{C}$), pH

and dissolved oxygen O₂ content (mg L⁻¹)) were conducted in intervals of roughly two weeks over the whole water column in Waschsee, Fohnsee and Eishaussee for almost one year. Although those lakes are hydrologically connected, they exhibit quite different mixing patterns (holomictic polymictic to meromictic dimictic). Also, local ground water was sampled at a shallow ground water well located in the southern part of Waschsee. δ¹⁸O of the individual samples was measured on an isotope-ratio mass spectrometer and the obtained depth profiles of δ¹⁸O were compared to those of the respective physical parameters measured concomitantly in the lakes.

In Waschsee, polymixis and the short residence time were visible in a uniform development of δ¹⁸O of all water layers and by the mean (-9.9‰) being very close to δ¹⁸O of local groundwater (-10.0‰).

δ¹⁸O values in the hypolimnion of Fohnsee followed a significant trend towards more depleted values during stratification, indicating subsurface inflow of groundwater. Entrainment of hypolimnetic waters during summer stratification as a result of a cooling period was indicated by δ¹⁸O in Fohnsee and Eishaussee. The meromictic condition of the western basin of Eishaussee was also obvious from the oxygen isotope signal of bottom water which was significantly different from δ¹⁸O in upper water layers over the whole study period and was not affected by the isotopic development in the upper water column.

In order to investigate the eutrophication history as well as the accompanying stratigraphic variations of δ¹³C and δ¹⁵N of SOM in the different basins of Eishaussee and in Fischkaltersee, three sediment cores were retrieved from the lakes and dated radiometrically by measuring the activity concentration of lead ²¹⁰Pb as well as caesium ¹³⁷Cs. Subsamples of the cores were used for measurements of δ¹³C and δ¹⁵N values of SOM and other sedimentary proxies (diatom index DI, ratio of total organic carbon to total nitrogen TOC/TN, %TOC, %TN) and the results were compared with multiannual data on the development of various water column parameters (total phosphorus TP, chlorophyll alpha chl a, temperature T, oxygen content %O₂, nitrate NO₃⁻, ammonium NH₄⁺).

In both lakes δ¹³C values of SOM were more depleted (as low as -38.8‰) than reported values for photoautotrophic biomass in many other lakes. In Fischkaltersee, the overall reaction of the δ¹³C signal to the documented process of eutrophication and artificial aeration was a continuous negative trend. In contrast, δ¹⁵N values of

SOM followed the trophic history of Fischkaltersee as documented by sedimentary DI quite closely (eutrophication: increase +3.4‰, trophic recovery: -2.7‰). The linear correlation of $\delta^{15}\text{N}$ values to nitrate utilisation in the epilimnion was rather weak ($R^2=0.33$).

In Eishaussee, sediment core parameters confirmed the impact of the eutrophication period around AD 1980 and revealed a trophic level increase probably due to anthropogenic impact around AD 1828, which also might have induced the meromixis present in the western basin (EHW), but not in the eastern basin (EHE). There is an offset in $\delta^{13}\text{C}$ of SOM between EHE and EHW (mean: +0.8‰ and +0.7‰ respectively) before as well as after the onset of meromixis while the overall reaction to both eutrophication episodes is a pronounced drop towards more negative $\delta^{13}\text{C}$ values (EHW: -2.6‰ and -3.5‰; EHE: -1.0‰ and -2.3‰) concordant in both cores, resulting in values as low as -37.7‰ (EHW) and -35.7‰ (EHE). In both cores from Eishaussee, the development of $\delta^{15}\text{N}$ of SOM is less conclusive and seems not to be directly influenced from the trophic evolution as indicated by the DI.

In conclusion, the results of this thesis revealed that $\delta^{18}\text{O}$ of water is a sensible indicator of key hydrologic processes present in the Osterseen lake district and can readily be integrated into routine water sampling.

The stratigraphic variations of $\delta^{13}\text{C}$ of SOM in Fischkaltersee and both basins of Eishaussee provide additional evidence for the practical relevance of the conceptual model published by Smith and Hollander (2001).

Zusammenfassung

Die Bedeutung der stabilen Isotope der Bioelemente für die Erforschung hydrologischer Kreislaufprozesse sowie der Untersuchung von Prozessen im Stoffkreislauf von Kohlenstoff und Stickstoff ist in vielen ökologischen Arbeiten gezeigt worden. Durch die Untersuchung stabiler Isotope von Wasserstoff und Sauerstoff als natürliche Markierung des Wassermoleküls konnten in der Untersuchung des Wasserkreislaufs Schlüsselerkenntnisse gewonnen werden, während stabile Isotope von Kohlenstoff und Stickstoff im sedimentierten organischen Material (SOM) mit großem Erfolg als Zeiger z.B. der historischen Entwicklung der Primärproduktion in Seen verwendet wurden.

Allerdings waren insbesondere beim Einsatz stabiler Isotope in der limnologischen Forschung einige zentrale Fragen bisher noch nicht ausreichend geklärt worden. Die Eignung des Isotopenverhältnissignals ($\delta^{18}\text{O}$) von Sauerstoff zur Untersuchung zentraler limnologischer Prozesse wie z.B. Entrainment tieferer, nährstoffreicher Wasserschichten während der Sommerstagnation oder der Vollzirkulation wurde noch nicht an Seen verschiedener Mixistypen untersucht. Ebenso beruht der weit verbreitete Einsatz der Isotopenverhältnissignale von Kohlenstoff ($\delta^{13}\text{C}$) und von Stickstoff ($\delta^{15}\text{N}$) zur Rekonstruktion der trophischen Vergangenheit in Seen meist auf der Annahme, dass die Biomasse der photoautotrophen Primärproduktion den Hauptanteil von SOM darstellt und dass deren Isotopensignal während der Sedimentationsphase weitgehend unverändert bleibt. Diese Hypothese wurde allerdings durch die Ergebnisse verschiedener publizierter Untersuchungen in Frage gestellt: Diese schreiben die Kontrolle über $\delta^{13}\text{C}$ und $\delta^{15}\text{N}$ von SOM eher dem Ausmaß von Anoxie in Wassersäule und Sediment zu, da hiervon die Intensität mikrobieller Umbauprozesse des organischen Materials vor und nach der Sedimentation gesteuert werde.

Primäre Zielsetzung der vorliegenden Arbeit war es daher, die Eignung des Isotopenverhältnissignals ($\delta^{18}\text{O}$) von Sauerstoff zur Untersuchung zentraler limnologischer Prozesse zu testen. Zudem sollten qualitative Daten bezüglich des Ansprechens von $\delta^{18}\text{O}$ auf verschiedene, im Osterseengebiet existierende limnologische Phänomene untersucht werden, darunter Polimixis im Waschsee, Meromixis im Eishaussee und der unterirdische Grundwasserzufluss im Fohnsee.

Die sekundäre Zielsetzung war es, ein konzeptuelles Modell, das die Kontrolle über $\delta^{13}\text{C}$ von SOM nicht nur bei der photoautotrophen Primärproduktion im Epilimnion, sondern vielmehr bei anaeroben methanogenen Prozessen sieht, am anhand des Fischkaltersees in der Praxis zu testen. Ebenso wurden die Auswirkung verschiedener Mixistypen und des Anoxisgrades im Hypolimnion auf die Erhaltung von $\delta^{13}\text{C}$ und $\delta^{15}\text{N}$ von SOM im Eishaussee untersucht. Daneben war ein weiteres Ziel dieser Arbeit, anhand bereits existierender Daten zur Eutrophierungsgeschichte von Fischkaltersee und Eishaussee zu untersuchen, welchen Effekt die jeweilige trophische Entwicklung auf den Verlauf verschiedener Zeiger im Sediment hatte.

Zur Erreichung der ersten Zielsetzung wurden an Waschsee, Fohnsee und Eishaussee über fast ein gesamtes Jahr Wasserprobenentnahmen und Tiefenprofilmessungen verschiedener physikalischer Parameter (Leitfähigkeit ($\mu\text{S cm}^{-1}$), Temperatur ($^{\circ}\text{C}$), pH und Gelöstsauerstoffgehalt (mg L^{-1}), jeweils des Wassers) durchgeführt. Obwohl diese drei Seen miteinander in Verbindung stehen, weisen sie sehr unterschiedliche Mixistypen auf (holomiktisch polymiktisch und meromiktisch dimiktisch). Zusätzlich wurden an einer Limnokrene im Süden des Waschsees Grundwasserproben entnommen. Mithilfe eines Isotopenverhältnis-Massenspektrometers wurde an den einzelnen Wasserproben $\delta^{18}\text{O}$ gemessen. Die so erhaltenen $\delta^{18}\text{O}$ -Tiefenprofile wurden den Tiefenprofilen der gleichzeitig gemessenen physikalischen Parameter gegenübergestellt.

Im Waschsee zeigte ein über alle Wasserschichten einheitliches $\delta^{18}\text{O}$ deutlich dessen Polimixis und die kurze Wasseraufenthaltsdauer an, was auch daran zu erkennen war, dass das Jahresmittel (-9.9‰) sehr nahe am im Grundwasser gemessenen Signal (-10.0‰) lag. Der Grundwasserzufluss ins Hypolimnion des Fohnsees war im $\delta^{18}\text{O}$ der untersten Wasserschichten an einem signifikanten Trend während der Stagnationsphase hin zu negativeren Werten zu erkennen. Dagegen wurde ein Entrainment tieferer Wasserschichten als Ergebnis einer Abkühlungsperiode während der Sommerstagnation im Fohnsee und Eishaussee nur anhand der Änderungen von $\delta^{18}\text{O}$ sichtbar.

Die permanente Meromixis des Eishaussees konnte dadurch bestätigt werden, dass sich $\delta^{18}\text{O}$ in den untersten Wasserschichten über den gesamten Untersuchungszeitraum vom Wert in den von der Durchmischung erfassten Bereichen unterschied und dem Signalverlauf nicht folgte.

Um sowohl die Eutrophierungsgeschichte als auch die begleitenden stratigraphischen Verläufe von $\delta^{13}\text{C}$ und $\delta^{15}\text{N}$ von SOM in Fischkaltersee und Eishaussee zu untersuchen, wurden aus den einzelnen Becken insgesamt drei Sedimentkerne entnommen. Die Datierung der Kernschichten erfolgte mittels Bestimmung der Aktivitätskonzentration von Cäsium ^{137}Cs und Blei ^{210}Pb . Teilproben der Kerne wurden für die Messung von $\delta^{13}\text{C}$ und $\delta^{15}\text{N}$ von SOM und anderen sedimentären Eutrophierungszeigern (Diatomeenindex DI, Verhältnis gesamter organischer Kohlenstoff (TOC) zu Gesamtstickstoff (TN) TOC/TN, Anteil TOC %TOC, Anteil TN %TN) verwendet und die Ergebnisse wurden mit mehrjährigen Datenreihen zur Entwicklung verschiedener Wassersäuleparameter verglichen (Gesamtphosphat TP, Chlorophyll alpha Chl a, Wassertemperatur T, Sauerstoffsättigung %O₂, Nitrat NO₃⁻ und Ammonium NH₄).

$\delta^{13}\text{C}$ von SOM war in beiden Seen negativer (bis zu einem Minimum von -38,8‰) als die meisten in andern Untersuchungen publizierten Werte für photoautotrophe Biomasse. Im Fischkaltersee zeigte $\delta^{13}\text{C}$ von SOM während des gesamten dokumentierten Prozesses von Eutrophierung und künstlicher Belüftung einen kontinuierlichen Trend hin zu negativeren Werten. Im Gegensatz dazu folgte $\delta^{15}\text{N}$ von SOM der Trophieentwicklung des Fischkaltersees (Eutrophierung: Zunahme um +3,4‰, Reoligotrophierung: -2,7‰) sichtbar, wobei aber die lineare Korrelation von $\delta^{15}\text{N}$ von SOM mit der Nitratnutzung im Epilimnion eher gering war ($R^2=0,33$)

Im Eishaussee bestätigten die verschiedenen Zeiger im Sediment einerseits eine bereits dokumentierte Eutrophierungsphase um 1980, zeigten aber andererseits auch eine noch undokumentierte Eutrophierungsphase um 1828 an. Diese ist vermutlich menschlichen Ursprungs und könnte die zeitgleich im westlichen (EHW), nicht aber im östlichen (EHE) Becken auftretende Meromixis ausgelöst haben. Hinsichtlich $\delta^{13}\text{C}$ von SOM gibt es einen Versatz zwischen den Signalen in EHE und in EHW vor (im Mittel +0,8‰) und nach (im Mittel +0,8‰ +0,7‰) dem Einsetzen der Meromixis in EHW. Auf die zwei Eutrophierungsepisoden ist die einheitliche Reaktion von $\delta^{13}\text{C}$ von SOM in beiden Kernen jeweils ein ausgeprägter Sprung zu negativeren Werten (EHW: -2,6‰ und -3,5‰; EHE: -1,0‰ and -2,3‰) was minimal zu Werten von -37,7‰ (EHW) and -35,7‰ (EHE) führt. Dagegen ist die Entwicklung von $\delta^{15}\text{N}$ von SOM in EHW und EHE schwieriger zu interpretieren, da sie anscheinend nicht direkt von der durch den DI angezeigten Trophieentwicklung beeinflusst wird. Die Ergebnisse dieser Arbeit zeigen, dass $\delta^{18}\text{O}$ ein empfindlicher Zeiger wichtiger

hydrologischer Prozesse in den Osterseen ist, der leicht in Routinewasserbeprobungen integriert werden kann.

Zusammenfassend stehen mit den Signalverläufen von $\delta^{13}\text{C}$ von SOM während der Eutrophierungsphasen in Fischkaltersee und Eishaussee zusätzliche Daten für eine Validation des von Smith und Hollander 2001 publizierten, konzeptuellen Modells zur Verfügung.

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Embedded publications

1. Entrainment, annual circulation and groundwater inflow in a chain of lakes as inferred by stable ^{18}O isotopic signatures in the water column

Emanuel Braig, Gerhard Welzl, Willibald Stichler, Uta Raeder and Arnulf Melzer
Journal of Limnology, 2010; 00(0): 278-286

Die Sauerstoffisotopensignatur $\delta^{18}\text{O}$ im Wassermolekül hat sich in zahlreichen Untersuchungen als verlässlicher Marker insbesondere bei der Erstellung von Wasserbilanzen von Seen erwiesen. Allerdings wurden $\delta^{18}\text{O}$ -Analysen bisher kaum eingesetzt, um zentrale limnologische Prozesse wie Vollzirkulation und Stagnation zu untersuchen. In dieser Arbeit wurden über ein Jahr (Mai 2008 – April 2009) der Verlauf von $\delta^{18}\text{O}$, Temperatur und Schmidtstabilität in der gesamten Wassersäule dreier benachbarter Seen der Osterseenkette untersucht, welche sich im Mixistyp deutlich unterscheiden (holomiktisch polymiktisch bzw. meromiktisch dimiktisch). Dabei wurde insbesondere das Ansprechen von $\delta^{18}\text{O}$ auf wichtige hydrologische Prozesse (Entrainment, Stagnation, Vollzirkulation und Grundwasserzufluss) und Wettereinflüsse (sommerliche Abkühlungsepisode, Eisbedeckung, Schmelzwasserzufluss) untersucht. Die Polymixis und der starke Grundwasserzufluss im Waschsee zeigten sich sowohl am zwar geringen, aber in allen Wasserschichten messbaren Verdunstungseffekt als auch in einer nur geringfügig vom lokalen Grundwasser abweichenden Signatur ($-10,01\text{‰} \pm 0,06$). Im Fohnsee konnte ein vermuteter aber bislang nicht durch Messungen belegter Grundwasserzufluss ins Hypolimnion anhand einer während der Sommerstagnation auftretenden Tendenz zu negativeren ^{18}O Werten bestätigt werden. In Fohnsee und Eishaussee waren Episoden von Entrainment während der Sommerstagnation an einer sprunghaften Anreicherung von ^{18}O in bis dahin dem Hypolimnion zuzurechnenden Wasserschichten erkennbar. $\delta^{18}\text{O}$ bestätigte auch die permanente Isolierung des Monimolimnions im meromiktischen Eishaussee über den untersuchten Zeitraum. Wir kommen zu dem Schluss, dass $\delta^{18}\text{O}$ ein exzellenter und zudem einfach interpretierbarer Marker für wichtige hydrologische Prozesse in Seen ist. Die Ergebnisse dieser Arbeit zeigen zudem wichtige Einschränkungen bezüglich der Interpretation von $\delta^{18}\text{O}$ von biotischen und abiotischen lakustrinen Zeigern zur Rekonstruktion von historischen Trends von $\delta^{18}\text{O}$ in Seen auf.

2. Fifty years of eutrophication and lake restoration reflected in sedimentary carbon and nitrogen isotopes of a small, hardwater lake (South Germany)

Emanuel Braig, Christoph Mayr, Gerald Kirchner, Andrea Hofmann, Uta Raeder and Arnulf Melzer

Journal of Limnology, 2013; 72(2): 262-279

In der Paläolimnologie werden die stratigraphischen Variationen von $\delta^{13}\text{C}$ und $\delta^{15}\text{N}$ des sedimentierten organischen Materials (SOM) häufig als Anzeiger für trophische Veränderungen verwendet, obwohl neuere Modelle gerade für eutrophe Seen den dominanten Einfluss auf diese Signale nicht der Intensität der Primärproduktion, sondern der sekundären Umsetzung von SOM in anaeroben Recyclingprozessen (z.B. Methanogenese) zuschreiben. Vor diesem Hintergrund wurden in der vorliegenden Arbeit die stratigraphischen Variationen von $\delta^{13}\text{C}_{\text{SOM}}$ und $\delta^{15}\text{N}$ in einem mittels ^{210}Pb und ^{137}Cs datierten, ca. 50 Jahre umfassende Sedimentkern aus dem Fischkaltersee untersucht und dessen sehr gut dokumentierter Eutrophierungsgeschichte gegenübergestellt. In diesem Zeitraum umfasst diese eine vergleichsweise rasche und extreme Eutrophierung (mesotroph – polytroph) als auch Meromixis und verschiedenste Sanierungsmaßnahmen (künstliche Belüftung und Polymixis, Phosphorausfällung und Einleitungssanierung). Mit Ausnahme eines initialen Anstiegs ist die Reaktion von $\delta^{13}\text{C}_{\text{SOM}}$ auf Eutrophierung, Meromixis und Sanierung ein stetiger negativer Trend (-3,7‰) mit den negativsten Signaturen (-38,8‰) im obersten Teil des Kerns, als bereits ein Rückgang der Trophie verzeichnet werden konnte. Da das Mn/Fe-Verhältnis eine permanente und zunehmende Anoxis im Sediment des Fischkaltersees anzeigt und $\delta^{13}\text{C}_{\text{SOM}}$ sich im propagierten TP-Bereich konsistent zum von Smith und Hollander (2001) publizierten Modell verhält, wird geschlussfolgert, dass im Fischkaltersee nicht die Intensität der Primärproduktion, sondern anaerobe Abbauprozesse $\delta^{13}\text{C}_{\text{SOM}}$ im Verlauf der Eutrophierungsphase kontrolliert haben. Die $\delta^{15}\text{N}$ -Werte reagieren auf den Trophieanstieg im Fischkaltersee mit einer Zunahme um +3,4‰, während der Rückgang der Trophie eine Abnahme um -2,7‰ zur Folge hat. Allerdings ist die Korrelation mit der Nitratnutzung im Epilimnion eher gering ($R^2=0,33$) und zwei Ausschläge zu negativeren $\delta^{15}\text{N}$ -Werten können mit dem Auftreten von Ammonium im Epilimnion in Verbindung gebracht werden, was deutlich zeigt, dass im relativ komplexen lakustrinen N-Kreislauf verschiedene Prozesse das sedimentäre $\delta^{15}\text{N}$ -Signal beeinflussen können.

3. Impact of anthropogenic eutrophication on sedimentary carbon and nitrogen isotope records from a meromictic and a holomictic basin of Lake Eishaussee (S-Germany)

Emanuel Braig, Christoph Mayr, Gerald Kirchner, Uta Raeder and Arnulf Melzer
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Die Verwendung von $\delta^{13}\text{C}$ - und $\delta^{15}\text{N}$ -Werten der SOM zur Rekonstruktion von Prozessen in der Wassersäule von Seen setzt voraus, dass die ursprüngliche Isotopensignatur auch nach Ablagerung der organischen Substanz im Sediment unverändert erhalten bleibt. Hierzu publizierte Untersuchungen liefern jedoch kein konsistentes Bild. Lehmann et al. (2004) zeigten aber, dass Quantität und Qualität diagenetischer Effekte auf $\delta^{13}\text{C}$ und $\delta^{15}\text{N}$ vom Grad der Anoxis im Hypolimnion und im Sediment abhängig sein können.

In dieser Arbeit wurde untersucht, wie das Eingangssignal eines einheitlichen Eutrophierungsprozesses in den $\delta^{13}\text{C}$ - und $\delta^{15}\text{N}$ -Werten der organischen Substanz der Sedimente eines holomiktischen (EHE) und eines meromiktischen (EHW) Beckens des Eishaussees widergespiegelt wird. Die geochemisch-biologische (%TN, %TOC, TOC/TN, Diatomeenindex DI) Untersuchung der beiden, mittels ^{210}Pb und ^{137}Cs datierten und mittels $\delta^{13}\text{C}$ parallelisierten Sedimentkerne ergab, dass der Eutrophierungsprozess im Eishaussee in zwei Phasen verlief: Die Meromixis in EHW ist vermutlich biogener Genese und wurde wohl durch die erste Eutrophierungsphase um 1828 ausgelöst, da der DI im EHW hier einen deutlichen Anstieg der Trophie anzeigt. Eine weitere Spitze des DI um 1986 stimmt gut mit TP-Daten und der allgemeinen Eutrophierung der Osterseenkette überein. Sowohl vor als auch nach dem Beginn der Meromixis in EHW gibt es einen $\delta^{13}\text{C}$ -Versatz zwischen EHE und EHW (+0,82‰ und +0,77‰), während die $\delta^{13}\text{C}$ -Werte in beiden Becken in den Eutrophierungsepisoden jeweils absinken und dabei minimal Werte von -37,65‰ (EHW) und -35,73‰ (EHE) erreichen. Daraus wird gefolgert, dass die $\delta^{13}\text{C}$ -Werte von SOM in beiden Becken des Eishaussees einerseits stärker von sekundären Recyclingprozessen wie der Methanogenese als von der Primärproduktion beeinflusst werden und andererseits, dass der Versatz in den $\delta^{13}\text{C}$ -Werten durch vom Grad der Anoxis gesteuerte Diageneseprozesse verursacht wird, welche im tieferen Becken EHW auch vor der Meromixis ausgeprägter waren. Die Entwicklung der $\delta^{15}\text{N}$ -Werte des SOM folgt in beiden Kernen in etwa der trophischen Entwicklung,

so dass ein kombinierter Einfluss der Nitratnutzung im Epilimnion und einer diagenetischen Denitrifikation wahrscheinlich ist.

Declaration of individual contribution

The three papers included in this cumulative PhD represent mainly my own work, which consisted of field analyses, sample preparation and isotope measurement, data processing, preparation of the graphs and writing of the first draft of the entire manuscripts. However, during entire process I recieved supporting contributions from various institutions or individual persons:

Paper 1: Arnulf Melzer, Uta Raeder and Willibald Stichler participated in the conceptual design and the interpretation of the results. Willibald Stichler and his team from the institute of Groundwater Ecology gave me full access to their equipment as well as their enormous know-how in the measurement of $\delta^{18}\text{O}$ and δD . Gerhald Welzl provided the calculations for the stability *sensu* Schmidt and helped preparing water balance equations in an earlier draft of the manuscript.

Paper 2: Arnulf Melzer, Uta Raeder and Christoph Mayr participated in the conceptual design. Christoph Mayr provided very helpful support throughout the entire process of sample collection, preparation, measurement, data processing and correcting my drafts of the manuscripts. XRF measurements were conducted as contract work by Christian Ohlendorf from GEOPOLAR, Bremen. Measurements of radioisotopes and the core chronology derived from it were provided as contract work by Gerald Kirchner and his team. Gerald Kirchner also contributed to the final draft of the respective chapters in the manuscript. Andrea Hoffmann wrote her bachelor thesis within this project and contributed diatom analyses, calculation of the index and sediment core lithology. Access to the extensive limnological dataset on water column parameters of Fischkaltersee during almost its entire history of eutrophication was unhesitantly provided by Brigitte Lenhart and Jochen Schaumburg.

Paper 3: Arnulf Melzer, Uta Raeder and Christoph Mayr participated in the conceptual design. Christoph Mayr provided very helpful support throughout the entire process of sample collection, preparation, measurement, data processing and correcting my drafts of the manuscripts. XRF measurements were conducted as contract work by Christian Ohlendorf from GEOPOLAR, Bremen. Measurements of radioisotopes and the core chronology derived from it were provided as contract work by Gerald Kirchner and his team. Gerald Kirchner also contributed to the final draft of

the respective chapters in the manuscript. Christina Beck and Ina Beyer wrote their bachelor thesis within this project and contributed diatom analyses and calculation of the index.

1 Introduction

1.1 Hydrologic, Carbon and Nitrogen Cycling Processes in Aquatic Environments

In the geosphere, large-scale cycling processes and in particular matter fluxes between the individual compartments of a cycle play a central role: The global water cycle for example represents the interconnection of all marine, atmospheric and terrestrial water resources and their exchange of water masses (Clark and Fritz 1997, Mook and De Vries 2000). The marine part of the cycle, consisting of the closed-loop circulation of evaporating seawater and its return flux by atmospheric precipitation over sea, accounts for some 90% of the total annual flux (Gat 1996). Only the remaining approx. 10% are available for the continental part of the cycle, but here they form all freshwater resources which are also interconnected by water mass fluxes. Eventually, all water temporarily fixed in glaciers, rivers, lakes and groundwater will return to the sea, closing the circle.

Because of the central role the continental part of the water circle has for many processes in our environment, decades of research have been dedicated to the identification and quantification of the fluxes between its individual compartments as well as to the investigation of key processes within them (e.g. Mook and De Vries 2000, Vörösmarty et al. 2000a, Huntington 2006). Recently, particular attention has been assigned to lakes as their universal distribution makes them ideal sentinels of processes associated with human-induced climate change while their sediment archives facilitate the calibration of various climate models on millennial timescales (e.g. Lücke et al. 2003, Jankowski et al. 2006, Williamson et al. 2009).

Aquatic carbon (C) and nitrogen (N) cycles in terrestrial waters have as well been thoroughly studied in the past, as they are limited only with respect to the involved compartments, but not regarding their potential impact on a global scale, given for example the ability of inland aquatic reservoirs to act as C and N sinks for their terrestrial counterparts (Cole et al. 2007, Heimann and Reichstein 2008, Tranvik et al. 2009).

Fixation of dinitrogen in the marine N cycle is a controlling factor for the global C assimilation as well and, thus, for atmospheric CO₂ levels, as it can considerably

increase productivity and biomass accumulation in N-limited systems (Vitousek et al. 1997).

Inland freshwater reservoirs are considered of minor importance in this respect (Wang et al. 2009), but it is an interesting fact that lakes, while accounting only for 0.8% of the surface of the oceans, retain the equivalent of more than one fourth of the annual atmospheric C buried in the sea (Einsele et al. 2001): the relative C-burial in lake sediments is generally more expressed than in the oceans or terrestrial sinks because of their higher productivity and thus faster sediment accumulation as well as low turnover rates after deposition (Cole et al. 2007). In particular small and medium sized lakes have been recognized as hot spots of C-cycling susceptible to anthropogenic impact (Tranvik et al. 2009), as relative C burial rates tend to increase with lake productivity (Cole et al. 2007). But the increasing bottom water anoxia associated with eutrophication can also result in elevated efflux of the important greenhouse gas methane CH_4 (Bastviken et al. 2004). Another consequence of increasing bottom water anoxia as fostered by eutrophication can be the elevated release of nitrous oxide N_2O , also a very potent agent of global warming, from water column or sediment denitrification (Naqvi 2000, Wang et al. 2009). The latter process is of particular importance in the rather complex aquatic N cycle, as it converts biologically available N into molecular forms inaccessible for most organisms, thus effectively eliminating it from aquatic reservoirs (Vitousek et al. 1997).

These examples illustrate that a holistic understanding of the transformation reactions and cycling processes of C and N in lakes is needed as well as an assessment of human impact on them in order to predict the effects of climate change correctly. Similarly, straightforward and reliable methods to assess hydrologic key processes in lakes are needed because the latter have been shown to be quite vulnerable to changes caused by climate change (e.g. Danis et al. 2004). In both marine and freshwater environments, many ecological as well as hydrological studies successfully employed natural occurring tracers to investigate those internal cycling processes as well as hydrologic key processes (Deniro and Epstein 1980, Imboden et al. 1984, Altabet et al. 1994, Kluge et al. 2007).

1.2 Applications of the Stable Isotope Method in Ecology and Hydrology

Phase transitions and biogeochemical reactions cause isotope fractionation (see chapter 1.3), which produces small deviations from the otherwise globally constant ratio of the isotopes of an element in the involved matter. As those deviations are - under defined conditions - constant and thus characteristic for specific processes, isotope fractionation occurring during various environmental pathways leaves an identifiable signal in the associated matter that can reliably be utilized for tracing the origin and path of a compound. Additionally mixing of two reservoirs with distinct isotope composition can be employed for quantification of mass fluxes. Thus, the measurement of the ratio of stable isotopes of the bioelements H, C, N, O has a long and successful history of application in the study of ecologic and hydrologic cycling processes and matter fluxes: Some examples include the formation of water balance equations employing the evaporative signal contained in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of water (e.g. Dinçer 1968; Gat and Bowser 1991, Blasch and Bryson 2007, Mayr et al. 2007, Yi et al. 2008), the disentanglement of soil respiration fluxes by $\delta^{13}\text{C}$ values of CO_2 (e.g. Braig and Ľupek 2010), as a indicator of the water availability status in grasslands (and thus its C sink / source activity), where the original $\delta^{13}\text{C}$ signature of browsed plants can still be identified in tail hair of grazing cattle (Schnyder et al. 2006), as a long-term record of the metabolic activity of pearl mussels by $\delta^{13}\text{C}$ values in the individual layers of their shells (Geist and Kühn 2005) as well as for the reconstruction of paleotemperatures by interpreting stratigraphic variations in $\delta^{18}\text{O}$ values in sedimental archives of diatom frustules (Leng and Barker 2006), ostracod shells (Grafenstein et al. 1999), cellulose (Wolfe et al. 2006), chironomid head capsules (Wooller et al. 2004) or variations of $\delta^{13}\text{C}$, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in tree rings of subfossil trees (Schleser et al. 1999, Mayr et al. 2003).

In the aquatic N and C cycles, key insights have as well been gained by the investigation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of various compounds: For well known reasons (O'Leary 1981), phytoplankton discriminates against ^{13}C during assimilation of aqueous CO_2 . As a consequence, variations in $\delta^{13}\text{C}$ values of organic matter deposited in the sediment have been interpreted as indicators of paleoproductivity (McKenzie, 1985; Hollander and McKenzie, 1991; Brenner et al., 1999), but also to

identify various OM sources (Mayr et al. 2005), to reconstruct changes in lacustrine cycling of nutrients (Heyng et al., 2012) or as proxies for ancient atmospheric CO₂ concentrations (Rau 1994, Kaufman and Xiao 2003).

$\delta^{15}\text{N}$ values of sedimental OM has also been used as a marker of aquatic paleoproductivity (Teranes and Bernasconi 2000, Altabet et al. 2001, Talbot 2001), although in lakes, the strong positive correlation between $\delta^{15}\text{N}$ of recently produced OM and the surface water nitrate NO₃⁻ concentration that has been proven to exist in marine environments (e.g. Sigman et al., 1999), is weakened by the fact that here P rather than N is the factor limiting primary production (Wetzel 2001).

Nevertheless, the combined use of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of sedimented OM has successfully been employed in multiple lacustrine studies reconstructing paleoproductivity (Hodell and Schelske 1998, Brenner et al. 1999, Meyers 2006, Drew et al. 2008). However, pivotal studies revealed that in the rather complex lacustrine C and N cycles processes not directly associated with the extent of productivity can significantly influence the primary signal of phytoplankton OM, either before (Hollander and Smith 2001) or after (Lehmann 2004) sedimental deposition. As this might represent a considerable limitation for the commonly applied interpretation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of OM as an indicator of paleoproductivity, field studies are needed to test the possible impact of these processes on the sedimentary isotope signals.

In the investigation of matter fluxes in the water cycle, the combined measurement of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of water has proven to be a very effective tracing technique, as both isotope signals contain information about the origin and the pathway of any water sample derived from precipitation. This arises from the fact that during the initial formation of precipitation by evaporation of ocean water, temperature and humidity dependent equilibrium and kinetic isotope effects fractionate against the heavy isotopes ¹⁸O and ²H (Craig and Gordon 1965, see Chapter 1.3.2). This applies also to other phase changes such as rain formation through condensation later on, so that inland waters tend to be depleted in both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in a very predictable way (Craig 1961, Daansgard 1964, Craig and Gordon 1965). As further evaporation, e.g. on the surface of a lake will lead to a qualitatively different but additional fractionation effect, the residual water will become enriched again in respect to deeper water layers or groundwater which are not affected by surface evaporation (Gat and Bowser 1991, Gibson 2002). As the impact of this evaporation

effect and thus the change in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values correlates with the water residence time in a lake and its inflow/evaporation ratio, the method of the combined investigation of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water has found widespread application in hydrology, especially in lake water balance investigations (e.g., Craig 1961; Dincer 1968; Gat and Bowser 1991; Mayr et al. 2007; Yi et al. 2008).

However, despite the potential of the method to identify and trace different water masses in a lake, the information contained in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values about the degree of stratification or mixing in the water column has been used only as a by-product of water balance investigations and not directly as a method for tracing limnological key processes such as annual overturn, subsurface groundwater inflow and entrainment of bottom waters (e.g. Gupta and Deshpande 2004, Delalande et al. 2005, Mayr et al. 2007, Caliro et al. 2008, Hofmann et al. 2008, Stichler et al. 2008).

1.3 Stable Isotopes of the Bioelements in Aquatic Environments

1.3.1 Stable Isotope Basics, Fractionation and Mixing

Almost every chemical element E exists in several forms that exhibit no other difference from each other than the amount of neutrons N present in their nucleus (Fry 2006). While the assignment of a given atom to an elemental class (and its chemical properties) is defined by its number of protons (atomic number Z), atoms of the same Z can differ in N . As the mass number A of an atom is the sum of Z and N , isotopes of one element differ in their atomic mass A (Unkovich et al. 2001):

$${}^A_Z E_N \quad (1.1)$$

There are radioactive isotopes which are subject to radioactive decay and transformation and stable isotopes which are not. For the isotopes of the light bioelements ($Z \leq 20$) carbon, hydrogen, oxygen and nitrogen (Table 1) the highest atom stability is reached at a Z/N ratio close to 1 (Clark and Fritz 1997). As this equals also the highest probability for formation, the by far most abundant (>98.9%) index isotope of each element commonly exhibits equal numbers of protons and neutrons, while the other, much rarer stable isotopes of the respective element have a few protons more and are therefore referred to as heavy isotopes (Auerswald et al. 2005).

Although this mass difference is often minor in absolute values and thus seemingly negligible, it is relatively large in case of the light bioelements and therefore has a pronounced effect on the physical properties of the respective isotopes. Because of the resulting differences in mobility and binding energy (Mook 2000, Aggarwal et al. 2005), isotopes and in particular molecules containing different isotopes (isotopomers) will behave differently in a variety of environmental processes, e.g. phase transformations or chemical reactions.

The so-called isotope fractionation (Urey 1947) during various processes produces the observable natural range of stable isotope ratios (see Table 1) and leaves an identifiable signal in the associated matter, while mixing of two isotopically distinct reservoirs equalizes the effects of fractionation (Fry 2006). Both processes can reliably be utilized for tracing the path of a given compound or for mass balance

estimations in the respective matter cycles. For this purpose, changes in abundance of the heavy isotope are analyzed, which by convention are expressed as either % of heavy isotope or as the ratio R relative to the abundance of the index isotope. Because changes in R caused by natural isotope effects are typically very small and in order to make measurements of R easily comparable, the δ notation has been introduced for stable isotopes (Craig 1961), where R in the sample is normalized to R in an internationally valid standard, multiplied by 10^3 and expressed in permil:

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \cdot 1000 \text{‰} \quad (1.2)$$

Thus, a negative δ value signifies that there is less of the heavy isotope in a sample compared to composition of the international standard, which in most cases has been chosen to represent R of the largest terrestrial reservoir of the respective element, e.g. the ocean for $\delta^{18}\text{O}$ or δD (Gat 1996). In the isotopic range of natural samples the relation between δ values and %heavy isotope is quasi-linear (Fry 2006).

Element	Stable isotopes	mean global abundance [%]	Standard (name/R= $\frac{[\text{heavy isotope}]}{[\text{index isotope}]}$)	δ notation	Range of δ values in natural abundance (‰)
Hydrogen Deuterium	^1H $^2\text{H} = \text{D}$	99,985 0,015	V-SMOW 0,00015576	δD or $\delta^2\text{H}$	700
Carbon	^{12}C ^{13}C	98,89 1,11	V-PDB 0,0111802	$\delta^{13}\text{C}$	110
Nitrogen	^{14}N ^{15}N	99,64 0,36	AIR-N ₂ 0,0036782	$\delta^{15}\text{N}$	90
Oxygen	^{16}O ^{18}O	99,76 0,20	V-SMOW 0,0020052	$\delta^{18}\text{O}$	100

Table 1: Isotopes of the bioelements, their mean global abundance, the respective international standard and the delta notation. V-SMOW: Vienna Standard Mean of Ocean Water; V-PDB:

Vienna Pee-Dee Belemnite; AIR-N₂: atmospheric nitrogen. ¹⁷O has been omitted from this overview, as its isotope effects parallel that of ¹⁸O at 1/10 extent (Gat 1996) and is not investigated as a rule in the environmental sciences. As well, other standards used in the measurement of δ¹⁸O (i.e. V-PDB) are not shown. Modified from Unkovich 2001, Auerswald et al. 2005 and Fry 2006

There are kinetic, essentially unidirectional fractionation processes as well as equilibrium reactions, where transformation can occur in both directions. As a general rule, most enzymatic reactions and therefore the associated biological C and N transformations are kinetic reactions, in which molecules containing the light isotope react more frequently (Fry 2006). Therefore, molecules bearing the light isotope will enrich in the formed product compared to the initial composition of the substrate. While the absolute difference of substrate and product in ‰ is commonly denoted by a capital Δ, fractionation can as well be expressed as fractionation factor α_k of kinetic reactions (Gat 1996, Fry 2006):

$$\alpha = \frac{k_L}{k_h} \quad (1.3)$$

where k_L and k_H represent the reaction rates of the isotopomer containing the light and the heavy isotope respectively. While Δ is defined as (Fry 2006):

$$\Delta = (\alpha - 1) \cdot 1000 \quad (1.4)$$

It has to be noted that in hydrology another definition is commonly used for indicating fractionation factors for equilibrium reactions, then denoted as α* (Gat 1996, Mook 2000, Gibson et al. 2002):

$$\alpha = \frac{R_{Substrate}}{R_{Product}} \quad (1.5)$$

Building on the latter definition of α, Δ can also be given as the isotope enrichment or depletion ε with the definition (Mook 2000):

$$\varepsilon = (\alpha - 1) \cdot 1000 \quad (1.6)$$

For equilibrium reactions, where isotope fractionation can occur in both the forward as well as the backward reaction and the resultant R in both phases depends only on the vapour pressure ratio of the respective isotopomers, the overall fractionation factor is given by the ratio α of the forward reaction to α of the backward reaction (Fry 2006):

$$\alpha = \frac{\alpha_{Forward}}{\alpha_{Backward}} \quad (1.7)$$

A rule applicable to most equilibrium reactions is that heavy isotopes concentrate in the phase where molecule bonds are strongest (e.g. the liquid phase for water), as they exhibit higher zero-point energies and thus higher binding energies than their light counterparts (Gat 1996, Fry 2006).

It is a characteristic of so-called non-equilibrium (Mook 2000) reactions relevant for many ecologic fractionation processes that the formed product is immediately removed from the system. When R of the instantaneously removed product is always formed in thermodynamic equilibrium with R in the reservoir, the process qualifies as a Rayleigh distillation, where R in the remaining substrate can be described as (Clark and Fritz 1997):

$$R_{S,i} = R_{S,0} * f^{(\alpha-1)} \quad (1.8)$$

while R in the formed product is (Lehmann 2002):

$$R_{P,i} = R_{S,0} * \left(\frac{1 - f^\alpha}{1 - f} \right) \quad (1.9)$$

where $R_{S,0}$ represents R of the substrate at the start of the reaction, R_P R of the formed product, f the remaining mass of the substrate after the time i and α the respective equilibrium fractionation factor. Rayleigh distillation plays a central role in many environmental isotope fractionation processes, for example during the initial assimilation of C and N in the euphotic zone as well as during the process of rainout in the formation of precipitation and thus, for the initial R of all inland waters derived from it (Gat 1996).

As introduced above, equations describing the process of mixing of two reservoirs of sufficiently distinct R have successfully been employed to establish isotope-mass balances in a broad variety of applications, for example in the estimation of $\delta^{13}\text{C}$ of ecosystem respiration by so-called Keeling-plots (e.g. Yakir and Sternberg 2000, Pataki 2003) as well as for inflow/evaporation estimation in lacustrine environments (Yehegdo 1997, Turner 2006, Mayr 2007). For water mass balance investigations, this can be described as (Gibson et al. 2002):

$$\frac{d(V\delta_L)}{dt} = I\delta_I - Q\delta_Q - E\delta_E \quad (1.10)$$

where V ist the volume of the reservoir, t ist he time, dV is the change in volume over a time interval dt, I is combined surface and subsurface inflow, Q is combined surface and subsurface outflow, E is evaporation and $\delta_L, \delta_I, \delta_Q$ and δ_E are the isotopic compositions of the reservoir, inflow, outflor and evaporative flux, respectively.

1.3.2 Isotope Effects in the Water Cycle

In general, precipitation is depleted in the heavy isotopes D and ^{18}O compared to the isotopic composition of ocean water, while stagnant inland water bodies such as lakes are enriched vs. their supplying inflow, e.g. surface runoff or groundwater (Gat 1996). It has been a key finding for isotope hydrology by Harmon Craig in 1961 that in global precipitation and thus, all continental water resources directly derived from it, $\delta^{18}\text{O}$ and δD show a strong linear correlation that can be described by:

$$\delta\text{D} = 8 * \delta^{18}\text{O} + d \quad (1.11)$$

with $d \approx 10$ later named the deuterium excess (Dansgaard 1964), which is a non-linear excess of D resulting from the higher relative diffusivity of the isotopomere $\text{D}^1\text{H}^{16}\text{O}$ over $^1\text{H}_2^{18}\text{O}$ (Clark and Fritz 1997) during the initial evaporation of ocean water (Gat 1996). The corresponding graph has later been named the global meteoric water line GMWL, as it represents the mean of many slightly different local or regional MWLs.

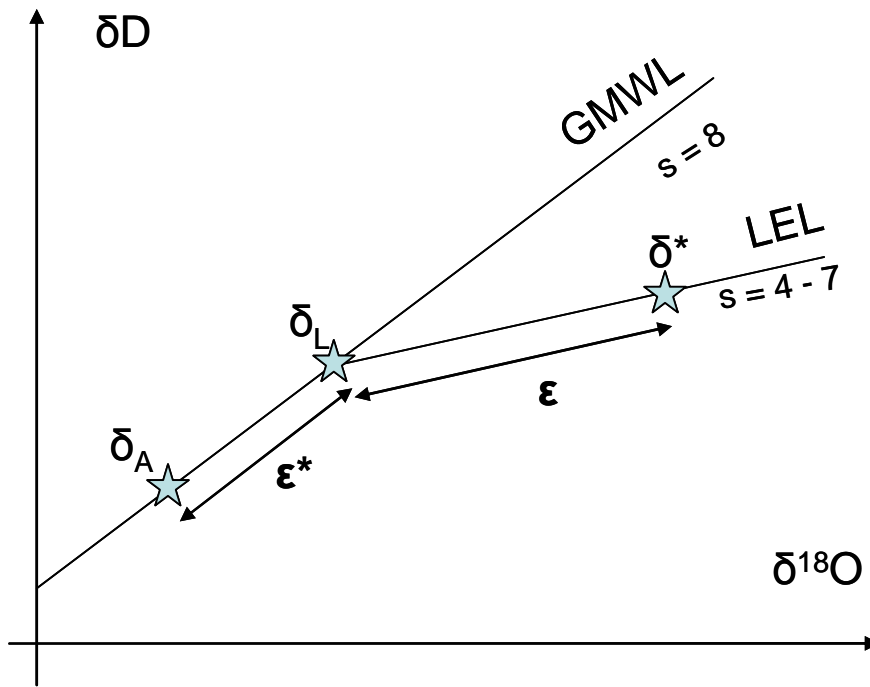


Figure 1: The global meteoric water line (GMWL) in δD vs $\delta^{18}O$ space with a mean elevation (s) of 8. The local evaporation line (LEL) usually exhibits a lesser s of 4-7. Subscripts A refer to air humidity, L to lake water. δ^* represents the isotopic equilibrium value, ϵ^* the equilibrium separation factor, ϵ the net fractionation factor. Modified after Gibson et al. 2002.

The process controlling the GMWL is the formation of precipitation out of atmospheric moisture by condensation (Gat 1996), which represents a Rayleigh distillation occurring in a vapor/liquid equilibrium (with a few well known exceptions), so the respective equilibrium fractionation value ϵ^* can be applied. For the normal temperature range precipitation is formed in, the ratio of ϵ^*D to $\epsilon^*^{18}O$ is approximately 8, resulting in a mean elevation of the GMWL of 8, while the absolute depletion in ^{18}O and D is mainly a function of near-ground temperature during rainout (Gat 1996). The latter translates into an altitude effect, a continental effect as well as a latitude effect (Dansgaard 1964), all of which have been successfully used for the identification of different water masses in numerous investigations (e.g. Bowen 2005, Gourcy 2005, Blasch and Bryson 2007, Gibson 2008). Eventually, this precipitation with its distinct isotope signal δ_i will supply inland surface waters such as lakes, where on their very surface the water becomes subject again to evaporation, resulting in an enrichment of the heavy isotopes. The net fractionation ϵ of this evaporation is the combined result of kinetic as well as equilibrium processes as described by the boundary layer flux model developed by Craig and Gordon (1965):

$$\varepsilon = \varepsilon^* + \varepsilon_K \quad (1.12)$$

with ε^* as the equilibrium separation factor and ε_K the kinetic fractionation factor both given separately for oxygen and hydrogen (Gibson et al. 2002). While ε^* , describing the equilibrium fractionation between water surface and the saturated boundary layer, is again a function of ambient temperature (Gonfiantini 1986, Horita and Wesolowski 1994), ε_K represents the kinetic fractionation during the evaporation from the saturated boundary layer into the turbulent atmosphere and is mainly dependent on atmospheric relative humidity h (Gibson 2002):

$$\varepsilon_K = C_K(1 - h) \quad (1.13)$$

C_K is a constant derived from the ratio D of the molecular diffusion coefficients of the respective isotopomers of water (14.3‰ and 12.5‰ for oxygen and hydrogen respectively, Gionfiantini 1986). Because of the additional kinetic fractionation term of ε_K and the similarity of the C_K constants, surface waters subject to the same evaporation conditions (humidity, temperature and isotopic composition δ_a of atmospheric moisture) will plot in δD vs. $\delta^{18}O$ space on the same line, which exhibits slightly lower slopes ranging from 4 – 7 and is referred to as Local Evaporation Line LEL. The exact slope of the LEL is given by (modified after Gat 1996):

$$S_{LEL} = \frac{[h(\delta_A - \delta_L) + \varepsilon]_{2H}}{[h(\delta_A - \delta_L) + \varepsilon]_{18O}} \quad (1.14)$$

where δ_A is the isotopic composition of atmospheric moisture and δ_L that of the inflow supplying the lake. While δ_L is given by the intersection of LEL and GMWL, δ_A is often calculated from δ_P of local precipitation, as both are assumed to be in isotopic equilibrium (Gat and Bowser 1991). The degree of enrichment along the LEL is proportional to the fraction of water lost by evaporation relative to inflow (Gibson 2002) and thus an indicator of water retention time of a lake. In a coupled evaporative system such as a string of sequentially troughflown lakes, evaporation enrichment in the lake surface water can proceed maximally to the point where isotopic equilibrium with atmospheric moisture is reached ($\delta^* = \delta_a + \varepsilon/h$, Dinçer

1968). Additionally, the isotope balance approach can give a useful estimate of the ratio of evaporation to inflow in so-called throughflow lakes (Gibson et al. 2002). These lakes are assumed to be in hydrologic steady state, so that the inflow I is balanced by the combined output of liquid outflow and evaporation E (Mayr et al. 2007) with δ_L here representing the equilibrium isotope ratio of the lake water:

$$\frac{E}{I} = \frac{1-h}{h} * \frac{\delta_L - \delta_I}{\delta^* - \delta_L} \quad (1.15)$$

1.3.3 Isotope Effects in the Lacustrine C Cycle

In lacustrine C isotope cycling, photoautotrophic primary production and the associated isotope fractionation during C uptake from the dissolved inorganic carbon DIC pool play a pivotal role. From this perspective, the isotopic composition of the surface water DIC pool (consisting of the components of the carbonate balance, CaCO_3 , HCO_3^- and CO_2^{3-}) can be seen as the starting point, setting the basis for further isotope effects. The initial value of $\delta^{13}\text{C}$ of DIC, which is visible before the onset of the primary production season (Zohary et al. 1994, Lehmann et al. 2004), will reflect the weighted mean of all internal and external inorganic carbon sources (Gu et al. 2004), the latter including atmospheric CO_2 , carbonate weathering and terrestrial OM (see Figure 2). In general, aqueous CO_2 is in isotopic equilibrium ($\epsilon = -1.1\text{‰}$, O`Leary 1988) with atmospheric CO_2 , which currently exhibits $\delta^{13}\text{C}$ values of -8.00‰ , (Bowling et al. 2008). In areas with carbonate bedrock of marine origin, weathering and runoff will introduce considerable amounts of DIC close to the standard V-PDB which by definition has a $\delta^{13}\text{C}$ value of 0‰ (Clark and Fritz 1997). In contrast, respiration of OM can potentially induce a negative signal to $\delta^{13}\text{C}$ of the lacustrine DIC pool (Rau 1978), because, dependent on the plant species and thus the enzymes responsible for the rate-limiting step during the photoassimilation (Rubisco in C_3 plants and phosphoenolpyruvate (PEP) carboxylase in crassulacean acid metabolism (CAM) and C_4 plants), the associated kinetic fractionation (mean $\epsilon = -20\text{‰}$ for C_3 , -4‰ to -6‰ for C_4 and -4‰ to -20‰ for CAM) will result in different $\delta^{13}\text{C}$ values in the formed OM of ca. -28‰ in C_3 , -14‰ in C_4 and -10‰ to -20‰ in CAM plants (O`Leary 1988, Unkovich 2001). Water pH controls the DIC species available

for C uptake by phytoplankton, which can be important for $\delta^{13}\text{C}$ of particulate OM POC as there is a difference of ca. +9‰ between aqueous CO_2 and HCO_3^- resulting from equilibrium fractionation (O'Leary 1988, Lehmann et al. 2004) and extensive CO_2 withdrawal as during periods of high assimilation rates is known to elevate the pH over 10, where DIC consists only of HCO_3^- (Wetzel 2001). As described above, phytoplankton, which is of the C_3 type (Meyers and Lallier-Vergès 1999) discriminates against ^{13}C during C assimilation, resulting in a progressive enrichment of ^{13}C during the consumption of the surface water DIC pool, which in turn will be visible in the subsequently produced POC_{PP} in the epilimnion as well as in its sedimental remains. Therefore, stratigraphic increases in $\delta^{13}\text{C}_{\text{TOC}}$ of SOM have widely been interpreted as indicators of increased paleoproductivity (McKenzie, 1985; Hollander and McKenzie, 1991; Brenner et al., 1999).

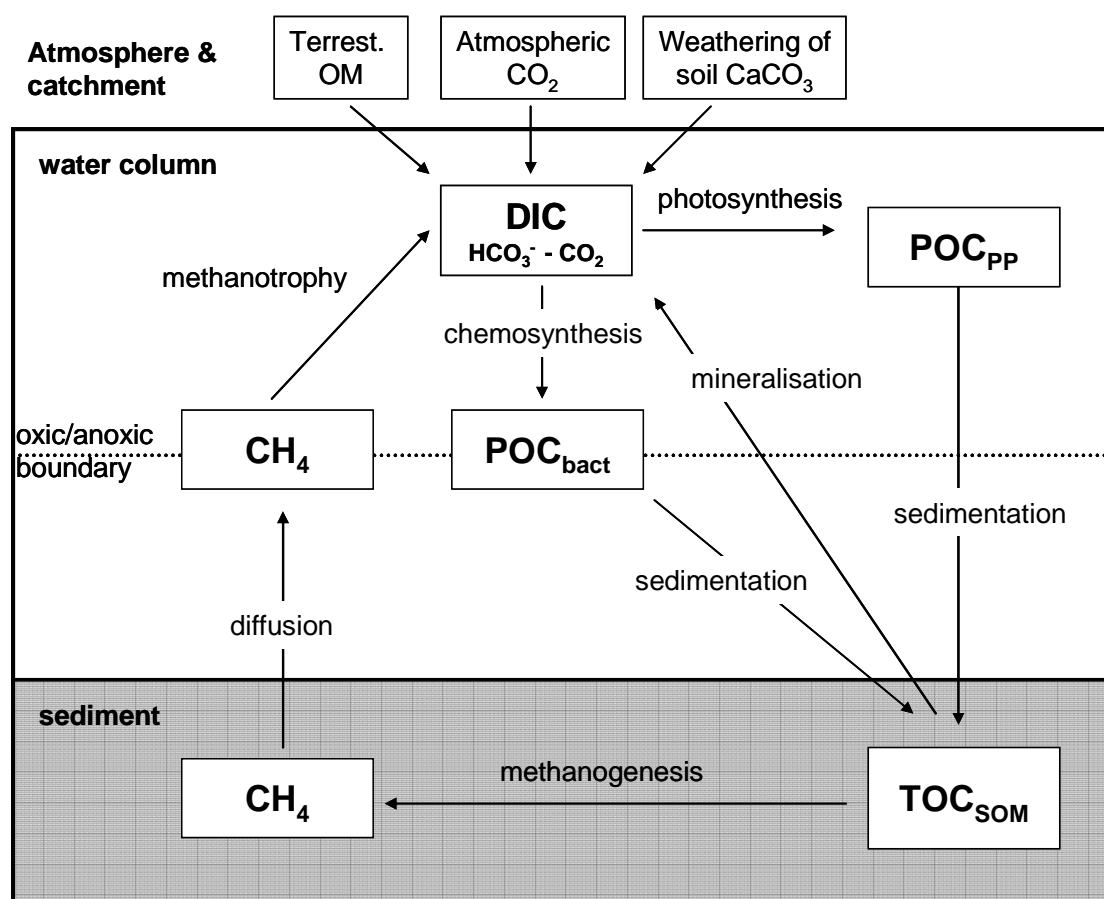


Figure 2: The lacustrine C cycle including terrestrial OM, atmospheric CO_2 and weathering of soil calcium carbonate CaCO_3 as input fractions from atmosphere & catchment. In the water column section, DIC HCO_3^- - CO_2 refers to the components of the carbonate balance, hydrogen carbonate ion HCO_3^- and carbon dioxide CO_2 . POC_{PP} and POC_{bact} refer to particulate organic carbon of photoautotrophic or bacterial origin. In the water column as well as the sediment section, CH_4 stands for methane and TOC_{SOM} for total organic carbon of sedimented organic matter. Modified after Hollander and Smith 2001.

However, despite an obligate enzymatic fractionation of -28‰ during C_3 carboxylation (O'Leary 1988) the effective carbon isotope fractionation between phytoplankton OM and DIC is not constant but can decrease during the productive season (Zohary et al. 1994, Hodell and Schelske 1998, Lehmann et al. 2004). It has been shown that this is controlled mainly by decreasing availability of dissolved CO_2 as well as changes in C uptake efficiency and – with the pH increasing with the intensity of CO_2 withdrawal - the use of the more abundant HCO_3^- as C source (Lehmann et al. 2004). Additionally, internal inputs to the DIC pool can include significant amounts of C from various chemoautotrophic as well as in particular heterotrophic sources (Fallon et al. 1980, Hadas 2001, Hollander and Smith 2001, Camacho 2001, Casamayor 2012). This is potentially of great importance for $\delta^{13}C$ of DIC, as both bacterial POC as well as biogenic methane are commonly considerably depleted in $\delta^{13}C$ (Woltemate 1984, Whiticar 1986, Whiticar 1999).

1.3.4 Isotope Effects in the Lacustrine N Cycle

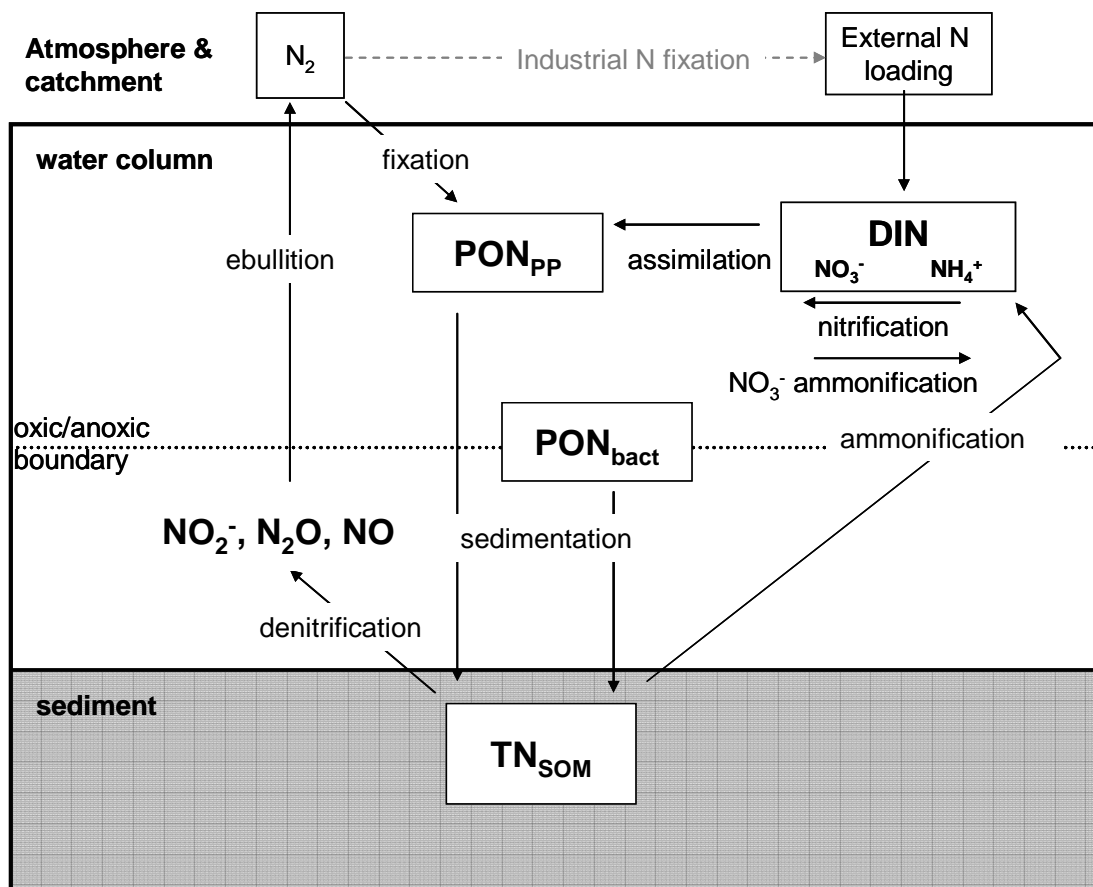


Figure 3: the lacustrine N cycle including input fractions from atmosphere & catchment such as atmospheric dinitrogen as well as external input of various molecular nitrogen. In the water column section, PON_{PP} and PON_{bact} refer to particulate organic nitrogen of photoautotrophic

or bacterial origin. Dissolved inorganic nitrogen DIN includes nitrate NO_3^- and ammonium NH_4^+ , while subscripts NO_2^- , N_2O and NO refer to nitrite, nitrous oxide and nitric oxide respectively. In the sediment section, TNSOM refers to total nitrogen of sedimented organic matter. Modified after Talbot 2001.

The relatively large variability of $\delta^{15}\text{N}$ values in lakes is caused by the many N forms available in the lacustrine N cycle as well as by the multitude of fractionation effects associated with the interconnecting biogeochemical pathways. Similar to DIC in the C cycle, the isotope composition of the dissolved inorganic N (DIN) pool can be seen as a baseline for lacustrine N fractionation. Phytoplankton discriminates against the heavier isotope during N uptake as well (Sigman et al. 1999), resulting in corresponding ^{15}N enrichment in surface water DIN during the productive season (Lehmann 2004). The associated fractionation effect is known to vary for different species ($\epsilon = -1.0\text{‰} \pm 0.9$ for diatoms and $\epsilon = -3.4\text{‰} \pm 0.4$ for green algae, Lehmann et al. 2004) and with the N form absorbed ($\epsilon = -10\text{‰}$ during NH_4^+ , -4‰ to -5‰ during nitrate NO_3^- uptake, Cifuentes et al. 1993), but in lakes where photoautotrophic production is the primary control of $\delta^{15}\text{N}$ of DIC and the surface water DIN pool is consumed to a sufficient extent, periods of elevated primary productivity will in turn be visible in an increase of $\delta^{15}\text{N}$ of the particulate organic nitrogen of photoautotrophic origin PON_{PP} subsequently produced and deposited in the sediment (e.g. Teranes and Bernasconi 2000).

In analogy to DIC, DIN reflects the weighted mean of all input fractions, but here those inputs can exhibit considerable variability in their isotopic composition, thus potentially overruling the signal of primary productivity: In contrast to CO_2 for DIC, atmospheric dinitrogen N_2 (representing the largest terrestrial N reservoir) is not accessible to most organisms and can only be integrated into the biologically available aquatic DIC pool by fixation, either by diazotrophic bacteria capable of breaking up the triple bond (e.g. cyanobacteria) or by external loading of bioavailable N from industrial fertilizers. The latter can be derived from production of ammonia NH_3 as a fertilizer in the Haber-Bosch process, which has reached more than twofold the extent of biological N fixation (Galloway et al. 2002, Galloway et al. 2008, Vitousek et al. 2013). As the associated isotope fractionation is only minor (cyanobacteria: $\epsilon = \pm 0\text{‰}$ Gu 2004, industrial N fixation: $\epsilon = \pm 2\text{‰}$, Bateman and Kelly 2007), in particular increased sedimentation of cyanobacterial biomass can have a significant influence on $\delta^{15}\text{N}$ of the total nitrogen content of SOM TN_{SOM} (e.g. Brenner 1999). On the other hand, external N loading derived from manure or human sewage

can induce considerable amounts of DIN extremely enriched in ^{15}N to a lake (+10 to +80‰, Auerswald et al. 2005), as these substances are subject to land-based denitrification. Denitrification in the water column and in the sediment is another key process in the lacustrine N cycle, as it not only effectively removes bioavailable N from the system, but also produces an expressed enrichment of ^{15}N (+14 to +26‰, Teranes and Bernasconi 2000) in the remaining DIN pool. As well, sedimentation of heterotrophic biomass can influence $\delta^{15}\text{N}$ of TN_{SOM} , as there is an increase of 3 to 4‰ in $\delta^{15}\text{N}$ with every trophic level (Deniro and Epstein 1981, Peterson and Fry 1987) and there exists conflicting evidence about the influence of diagenetic processes on $\delta^{15}\text{N}$ of TN_{SOM} (Hodell and Schelske 1998, Lehmann 2002, Gälmann 2008).

1.4 Objectives of the thesis

The work within the present thesis is divided into two research topics. Firstly, the applicability of the oxygen isotope signature $\delta^{18}\text{O}$ of the water molecule for tracing of limnological key processes such as entrainment of hypolimnetic waters during stagnation or annual turnover was investigated. For most limnological studies it is vital to possess information about processes such as the extent of mixis or stratification or subsurface inflow of groundwater in sufficient temporal resolution. Despite this, the information of the evaporative signal of $\delta^{18}\text{O}$ has rarely been tested for this application, although it allows for an identification of different water masses in a stratified lake.

Within this research topic, the present investigation had the following objectives:

- To test the suitability of $\delta^{18}\text{O}$ for tracing of limnological key processes such as annual overturn, entrainment and ground water inflow under a broad range of mixis conditions.
- To collect qualitative information on the reaction of $\delta^{18}\text{O}$ to several limnological phenomena in the Osterseen lake district including polymixis in Waschsee, entrainment during summer stratification as well as ground water inflow in Fohnsee and meromixis in Eishaussee.

Within the second research topic the C and N isotope signals of SOM as well as the various influences on them were investigated. Those signals have been used for decades as indicators for paleoproductivity, as several investigations were able to show that the intensity of primary productivity can be the dominant control on these signals.

However, as only a minor part of the OM originating from primary production in the epilimnion is directly buried in the sediment (Lehmann et al. 2002), secondary anaerobic recycling processes can potentially leave a significant impact on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM (Hollander and Smith 2001). As well, it has been revealed partly by incubation experiments (Lehmann et al. 2002) that the degree of water column and sediment anoxia can significantly influence both the quality and quantity in which the primary signal of SOM changes during postburial diagenetic processes. As this might represent a major limitation for the widespread interpretation of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of SOM as an indicator of the extent of paleoproductivity, the possible effects of bottom

water anoxia on the isotopic signals of SOM have to be investigated, as it is a common phenomenon during eutrophication. Additionally, field studies are needed that test the practical relevance of the theoretical models introduced above.

Within this research topic, the present investigation had the following objectives:

- To test the conceptual model published by Smith and Hollander (2001) on the influence of anaerobic methanogenic processes on $\delta^{13}\text{C}$ of SOM in the case study of Fischkaltersee and to provide additional data on the reaction of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM to a broad range of well-documented eutrophication conditions.
- To test the applicability of $\delta^{15}\text{N}$ of SOM as a proxy indicator for surface water nitrate utilisation in Fischkaltersee.
- To reconstruct the eutrophication history of Eishaussee
- To explore the effect of different mixing types and thus, bottom water oxygenation conditions on the conservation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM in the meromictic as well as holomictic basin of Eishaussee.

2 Methods

2.1 Study area: The Osterseen Lake District

Located at the southern end of Lake Starnberg in Upper Bavaria, Germany, the Osterseen lake district (Figure 4) consists of 20 individual, but hydrologically interconnected lakes. The basins thus form a chain of lakes that extends mainly from South to North and drains into Lake Starnberg. Because of a synchronous formation process at the end of the last Glacial, the lakes share very uniform kettle-like basin morphology with the deepest point approximately beneath the centre of the lake surface.

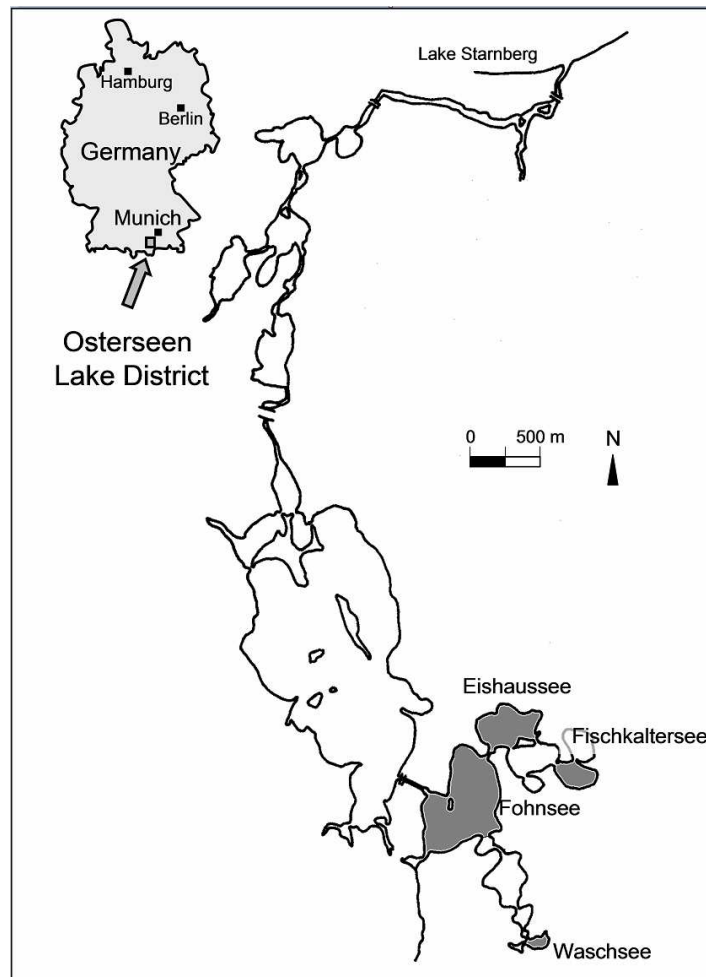


Figure 4: The Osterseen lake district. The investigated lakes Eishaussee, Fischkaltersee, Fohnsee and Waschsee are highlighted with a dark grey filling. Adapted from Raeder et al. 2009

Despite this uniformity in basin morphology and basic water chemistry the Osterseen exhibit both a considerable variety in mixis types (from holomictic

polymictic to meromictic dimictic) as well as an interesting history of anthropogenically induced eutrophication, which resulted in a broad range of trophic conditions (oligothrophic to polytrophic) because of its rather rapid and severe progress. As the impact of eutrophication was most expressed at the South and East end of the chain of lakes (i.e. Waschsee and Fischkaltersee) but spread in the basins downstream from there, the dilution of the nutrients formed a gradient of trophic conditions that still is present today.

The flowthrough pattern - and to some extent the variety in mixis types - is caused by the fact that the lakes are fed almost exclusively by subsurface inflow of groundwater, which is most expressed in the Southern part and has a noticeable effect on the hydrology of the respective lakes (Melzer 1976).

A major focus of limnological research at the Osterseen has been dedicated to the effects of the anthropogenically induced eutrophication on macroscopic aquatic plants (Melzer 1976, Schneider 2004) and phytoplankton (Raeder 1990). Both their well known basic limnology (e.g. Zorell 1943) as well as the gradient of a broad range of trophic conditions offers an ideal basis for comparative analyses and in particular for the establishment of new (Melzer 1976) and validation of existing (Raeder 1990) trophic reference systems. Additionally, because of the preconditions named above the Osterseen lake district offers the potential for testing the applicability of $\delta^{18}\text{O}$ as a tracer for basic hydrologic processes as well as an practical validation of recent theoretical models on the impact of eutrophication on $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of SOM under different mixis conditions.

However, the stable isotope method has only been applied in the Osterseen lake district to adress municipal ground water well supply issues (Eichinger 1993) as well as for an explorative investigation of water balance and food chain effects (Stichler and Fuentes, unpublished results) up to now.

2.2 Water column sampling, sample preparation and measurement of $\delta^{18}\text{O}$ and δD in water

As a consequence of the theoretic aspects of isotope fractionation in the water cycle described above, both stable isotope ratios of the elements of the water molecule should be identically suitable to describe key processes in the water column of lakes. Therefore, both $\delta^{18}\text{O}$ and δD of the individual water samples were measured in parallel in this thesis.

Water column sampling, which was intended to cover an entire seasonal cycle, was accompanied by synchronous depth profile measurements of water conductivity ($\mu\text{S cm}^{-1}$), temperature ($^{\circ}\text{C}$), pH and dissolved oxygen O_2 content (mg L^{-1}) mostly recorded in parallel by usage of a multi-parameter probe (WTW Multi 350i, Weilheim, Germany). Water samples were taken from the surface to the bottom of Waschsee, Fohnsee and Eishaussee in 2 m steps using a 2 L Ruttner water sampler (Hydrobios, Kiel, Germany) about every two weeks during the period between March 2008 and April 2009. As well, ground water from a limnocrone located at the south end of Waschsee was sampled on 4 occasions during the sampling period. Water samples were filled into polyethylene flasks immediately after retrieval and kept tightly sealed and stored at room temperature for isotope measurements. Both the oxygen as well as the hydrogen isotope ratio of the individual samples were measured separately on a isotope ratio mass spectrometer IRMS (Delta C, Finnigan MAT) after the respective sample preparation. For δD , preparation consisted of online quantitative reduction of sample aliquots ($2 \times 20 \mu\text{L}$) in an uranium oven (3 min, 800°C) to gaseous H_2 , which was then introduced into the IRMS (Mook 2000). For $\delta^{18}\text{O}$, sample aliquots (5 mL) were equilibrated online with an overlying CO_2 headspace for 5 – 6 h at 20°C , allowing for a predictable equilibrium fractionation between the aqueous and the gaseous phase, which was then introduced into the IRMS (Moser and Rauert 1980). In the ionisation chamber of the IRMS, the gaseous molecules are first ionized by electron impact ionisation, and then accelerated on a parabolic flight path in a strong magnetic field. Here, the mass differences of the ions (or ionized isotopomers) translate into different trajectories, resulting in a separation of the isotopes of an element present in the sample, which can be detected as the ratio of elementary charges at the targeted ion collectors (Clark and Fritz 1997). As these IRMS measurements are very precise but prone to drifting

effects, all mass spectrometers employ the parallel measurement of a working standard in between the actual samples. The working standard is of known and constant R and helps in correcting for drifting effects during measurements. For both the measurements of $\delta^{18}\text{O}$ and δD , internal reference standards calibrated to V-SMOW were used.

2.3 Sediment sampling, sample preparation and measurement of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM

In order to investigate the eutrophication history as well as the accompanying stratigraphic variations of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of SOM in Fischkaltersee and Eishaussee, sediment cores were retrieved from the deepest part of the respective basin using an UWITEC gravity corer (UWITEC, Mondsee, Austria). Cores were stored dark and cool (4°C) until sampling. Therefore, cores were split lengthwise in two and the surfaces of the respective half cores were photographed and described lithologically. After non-destructive X-ray fluorescence (XRF) scanning (Mo tube, 200 μm step size) with an ITRAX XRF core scanner (Cox Analytics, Mölndal, Sweden) (Lüder et al. 2006, Croudace et al. 2006), both half cores were sampled volumetrically in 1 cm steps and visible remains of landplants were removed. To determine dry density and the water content, the resulting subsamples were then weighted and freeze-dried. An independent age model for each core was established from measurement of the activity concentrations of ^{210}Pb and ^{137}Cs in the samples of one half core by following the protocol published by Nehyba et al. (2011). Afterwards, non-homogenized sample aliquots from several stratigraphic horizons were used for the establishment of a sedimental diatom index using standard techniques (Battarbee et al. 2001) Samples of the other half core were homogenized and used for isotope and elemental analyses. For the measurement of %TN and $\delta^{15}\text{N}_{\text{SOM}}$ an aliquot of ca. 8 mg of bulk sediment was weighed into tin capsules and combusted at 1080°C in an elemental analyzer (NC 2500, Carlo Erba, Milano, Italy) directly connected to an IRMS (DeltaPlus, Thermo-Finnigan, Waltham USA), as DIN is negligible fraction of sedimental matter in most lakes (Teranes 2001). This is different for measurements on OC in sedimental matter: especially in carbonate-rich basins, DIC is a major component of the sediment which has to be removed prior to measurements on OC, as it otherwise will adulterate both the measured % content as well as the $^{13}\text{C}/^{12}\text{C}$ ratio. For this, different acidification methods can be employed, but as sediment from

the Osterseen is rather rich in carbonate (>45%), an in situ treatment of ca. 3.3 mg of bulk sample with 3% hydrochloric acid at 80°C (Niewenhuize et al. 1994, Ryba and Burgess, 2002; Kennedy et al. 2005) was chosen, as other methods have been reported to fail in removing all inorganic carbon in the sample (Kennedy et al. 2005).

3 Entrainment, annual circulation and groundwater inflow in a chain of lakes as inferred by stable ^{18}O isotopic signatures in the water column

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Running title: Lake mixing processes inferred by oxygen stable isotopes

3.1 Abstract

The stable oxygen isotopic signature $\delta^{18}\text{O}$ of water has been proved to be a useful marker in hydrological lake studies. However, it is applied only sporadically to determine the extent of mixing and stratification, which is vital for all hydrological and limnological studies.

We present a study of the changes in $\delta^{18}\text{O}$, temperature and Schmidt stability in the water column of three adjacent lakes of very different mixing types (polymictic to meromictic) over almost one year (May 2008 to April 2009). The response of $\delta^{18}\text{O}$ to important hydrologic processes (entrainment, stratification, circulation, groundwater inflow) and weather influences (cooling period, ice cover and melt water inflow) is discussed. The lakes are part of the Osterseen chain of lakes south of Munich, Germany. Although hydrologically connected, these lakes show various mixing types (polymictic to meromictic) due to large differences in size, groundwater inflow and water renewal time. Polymixis and the strong subsurface inflow of groundwater Lake Waschsee ($25.6 \times 10^3 \text{ m}^3$) were indicated by the $\delta^{18}\text{O}$ signature throughout all water layers and by the mean overall signature (-9.94 ‰) being very close to $\delta^{18}\text{O}$ of local groundwater ($-10.01 \text{ ‰} \pm 0.06$). $\delta^{18}\text{O}$ signatures of the larger dimictic Lake Fohnsee ($2298.3 \times 10^3 \text{ m}^3$) revealed a highly significant trend towards lower values of $\delta^{18}\text{O}$ in its hypolimnion, indicating inflow of groundwater. A cooling period during the summer stratification characterised by high wind speeds resulted in a considerable drop of lake surface temperatures and Schmidt stability (up to 25 %) in Lake Fohnsee and Eishaussee and was followed by a deepening of the mixed upper water layer and entrainment of hypolimnetic water layers. This was clearly shown by a signal change in deeper water layers formerly constant in $\delta^{18}\text{O}$. The permanent meromixis present in Lake Eishaussee ($297.0 \times 10^3 \text{ m}^3$) could also be confirmed by isotope signatures, as bottom water layers remained significantly isolated in $\delta^{18}\text{O}$ from the remaining water column over the whole study period. We summarize that the oxygen isotopic signature of water is an easy to interpret, excellent indicator of important hydrologic processes in a lake and can readily be integrated into routine sampling. The present findings will further contribute to the analysis of hydrological data as well as to the interpretation of paleoclimatic reconstructions using proxies of lake water $\delta^{18}\text{O}$.

3.2 Introduction

The dimictic state with a pronounced thermal stratification of water during summer is considered a reference situation for the vast majority of lakes in temperate regions of low to mid altitude (Wetzel 2001).

Summer stratification has a drastic effect on nearly all biological, chemical and physical processes in a lake, especially on the trophic situation and primary production (MacIntyre 1993, Salmaso 2005). As the degree and the stability of the summer stratification are a function of density differences mainly dependent on water temperature and salinity (Chen & Millero 1986, Bohrer & Schultze 2009), many researchers only used the water temperature signal to study mixing in lakes (e.g. MacIntyre 1993, Ambrosetti *et al.* 2001). A good indicator for the extent of stratification in a lake is the stability index *S sensu* Schmidt (Kjensmo 1994), which is calculated from density differences in the water column. It is a measure of the energy that would be necessary to mix a thermally stratified lake so as to create a new isothermal state without further addition or loss of heat (Ambrosetti *et al.* 2001).

It is mainly dependent on surface water temperature (Barbiero *et al.* 1997), which in turn is strongly influenced by air temperature. Therefore, cooling periods within the summer stratified season can produce a considerable drop in stability, which may present a precondition for but not necessarily the result of wind-induced mixing in an isothermal epilimnion. Although having little or no effect on the physical properties, the latter can have a significant impact on the intensity of primary production, as it causes vertical entrainment and internal loading of Phosphorus to the epilimnion (Barbiero *et al.* 1997, Soranno *et al.* 1997, Carstensen *et al.* 2004).

The use of the stable isotopic signature of the elements of water as a marker of hydrological processes in lakes has a long and successful history: Since the initial description of the systematic variations in the isotopic composition of meteoric waters worldwide by Harmon Craig in 1961, the stable isotope method has found widespread application in hydrology, especially in lake water balance investigations (e.g. Craig 1961, Dincer 1968, Gat & Bowser 1991, Mayr *et al.* 2007, Yi *et al.* 2008).

Together, stable isotopes of hydrogen and oxygen form the different isotopomers of water ($^2\text{H}^1\text{HO} / ^1\text{H}_2\text{O}$ and $\text{H}_2^{18}\text{O} / \text{H}_2^{16}\text{O}$). Due to slight differences in their molecular diffusivity and saturation vapour pressure (Dincer 1968, Gibson *et al.* 2002), evaporation leads to heavy isotope enrichment of the remaining water.

Because of their position in the water cycle, inland waters tend to be depleted in the heavy isotopomers relative to the isotopic composition of sea water (Gat 1996). Accordingly, further evaporation leads to an amount of isotopic re-enrichment in the lake water representative for its respective balance of inflow and evaporation (Gat & Bowser 1991, Gibson *et al.* 2002, Mayr *et al.* 2007). The isotopic equilibrium value of a dimictic holomictic lake integrates over all hydrological influences and is only apparent during annual circulations (Gibson *et al.* 2002, Stichler *et al.* 2008). During summer stratification, the signal of isotopic enrichment due to evaporation on the lake surface is constrained to the mixed upper layer, while the signal in the hypolimnion remains constant or might even be subjected to a slight depletion proportional to subsurface inflow of groundwater with a more negative isotopic signature. An informative overview of these processes can be found in the introduction of Gibson *et al.* (2005).

Stable isotopes of oxygen and hydrogen are well suited for investigating lake stratification and circulation, since they can be easily integrated in routine water sampling. They are universally existent and therefore applicable when compared to the limits of artificial tracers (e.g. Holzner *et al.* 2009). Moreover, the response of the signal is highly specific and only occurs in the case of significant mass transport of water (Dinçer 1968).

Despite this, the information provided by the isotopic signal about the degree of stratification of the water column has been used rather hesitantly and only as a by-product of water balance investigations (e.g. Hostetler & Benson 1994, Gupta & Deshpande 2004, Delalande *et al.* 2005, Mayr *et al.* 2007, Caliro *et al.* 2008, Hofmann *et al.* 2008, Stichler *et al.* 2008).

Only recently, the potential of the oxygen stable isotopic signatures for studying stratification and turnover processes in lakes has been demonstrated by Perini *et al.* (2009), who used this signal for a qualitative estimation of the perennial development of circulation, stratification, and groundwater inflow in 6 Italian lakes.

Here, we describe the progressive annual changes (May 2008 to April 2009) of the oxygen isotopic signature in the water column of three adjacent lakes with different hydrology (polymictic to meromictic). The response of the signal to entrainment events and groundwater inflow is also discussed.

We show that the oxygen isotopic signature $\delta^{18}\text{O}$ of water is an easy to interpret, excellent indicator of important hydrologic processes in a lake and can readily be integrated into routine sampling.

3.3 Material and Methods

3.3.1 Study site

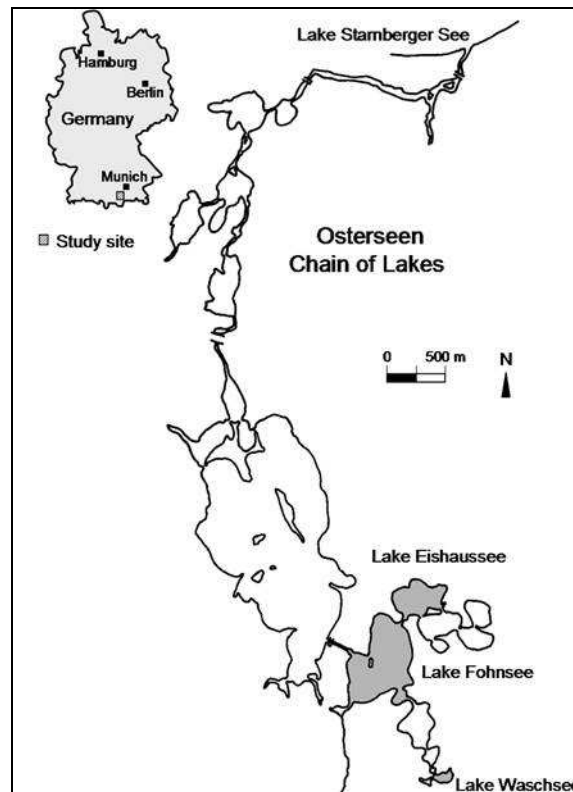


Figure 5: Outline map of the geographic location of the Osterseen chain of lakes. The investigated lakes are highlighted with an grey filling

The Osterseen chain of lakes (Figure 5) is located at the southern end of Lake Starnberg south of Munich, Germany. It consists of 20 individual, but hydrologically connected lakes. Formed after the rapid disintegration of the Würm glacier ice shield at the end of the last Ice Age, the lakes share a very similar kettle-like basin morphology with the deepest point beneath the centre of the lake surface (so called 'Toteisrestseen', Rothpletz 1917). The lakes are fed almost exclusively by subsurface groundwater inflow which in some lakes is quite strong and has a noticeable effect on hydrology and mixing type (Melzer 1976). Accordingly, water renewal time also varies from lake to lake.

In this study, the oxygen isotopic signal in the water column of three selected lakes was monitored over the course of almost one year (May 2008 to April 2009). Those lakes, namely Lakes Waschsee, Fohnsee and Eishaussee (Figure 5), differ markedly in size and hydrologic properties (see Table 2).

Table 2: Basic morphometric and hydrologic parameters characterizing the investigated lakes in the Osterseen chain of lakes with an elevation a.s.l of 594 m (data from Zorell (1943))

Parameters	L.Waschsee	L.Fohnsee	L.Eishaussee
surface area (m ²)	8500	211,900	34,148
volume (x 10 ³ m ³)	25.6	2298.3	297.0
max depth (m)	5.4	23.7	19.6
mean depth (m)	3.0	10.8	8.7
ground water inflow	very high	<i>significant*</i>	none
water residence time	<i>very low*</i>	<i>high*</i>	<i>very high*</i>
mixis type	polymictic	dimictic	dimictic
	holomictic	holomictic	meromictic

* as indicated by our results

3.3.2 Sampling and measurements

Conductivity ($\mu\text{S cm}^{-1}$) and temperature ($^{\circ}\text{C}$) profiles were taken in 2 m intervals at the deepest point of each lake with a multi-parameter probe (WTW Multi 350i). Measurements were carried out about every two weeks in the period from March 2008 to April 2009 (15 – 16 samplings). A lead weight (1.5 kg) was attached to the multi-parameter probe to avoid potential error in depth due to wind drift of the boat. The water samples for analysis of oxygen isotopic signature were taken in the same depths on the same occasion immediately after the temperature measurements, but not before 21.05.08 (11- 12 samplings). On 16.01.09, sampling was conducted under ice on Lakes Fohnsee and Eishaussee. For sampling, a 2 L Ruttner water sampler (Hydrobios) was used. Groundwater was sampled for oxygen isotope analyses at a

subaqueous ground water well close to the surface in Lake Waschsee on 4 occasions during the study period.

The oxygen isotopic ratio $R = {}^{18}\text{O}/{}^{16}\text{O}$ of the water samples was analysed at the Institute of Groundwater Ecology, Neuherberg, Germany with an isotope ratio mass spectrometer (Delta C, Finnigan MAT) following online-preparation by the $\text{CO}_2 - \text{H}_2\text{O}$ equilibration method (Moser & Rauert 1980). Presented values are the arithmetic mean of two independent measurements of the same sample, with the analytical precision (standard deviation of the mean) being always $< 0.1 \text{ ‰}$, in more than 70 % of measurements even better than 0.05 ‰ . They are reported as per mill in the delta notation against the international reference standard VSMOW (Vienna Standard Mean Ocean Water), where

$$\delta^{18}\text{O}_{\text{sample}} = (R_{\text{sample}} / R_{\text{standard}} - 1) * 1000. \quad (3.1)$$

Weather data were obtained from the weather station in Rothenfeld 21 km away (www.lfl.de/agm/).

3.3.3 Calculation of stability and statistical analysis

To account for the intensity of summer stratification, stability S *sensu* Schmidt as presented by Kjensmo (1994) was calculated for the whole water column of each lake for each sampling from March 2008 to April 2009. The density of water at each depth was calculated according to Chen & Millero (1986), conductivity was converted to salinity according to Boehrer & Schultze (2009).

Lake volume and area data were taken from a digital elevation model of all lakes produced by a sonar depth survey. They were also used to calculate volume-weighted means of the isotopic signature of all water layers of a lake at certain dates. A two-tailed T-Test was used to test the permanence of isolation of bottom waters (16 m to bottom) in Lake Eishaussee. In addition, a linear regression was conducted to analyse a trend to lower values during stratification (21.05.08 -18.11.08) in the hypolimnion of Lake Fohnsee (10 m – 22 m). All figures and calculations were done either with the free statistic software R (www.r-project.org) or with MS Excel 2003.

3.4 Results

3.4.1 Local Weather

Figure 6.a – c shows the development of the main climatic parameters air temperature [$^{\circ}\text{C}$], daily mean of wind speed [ms^{-1}] and daily sum of solar radiation [Wm^{-2}] in the area of the study site for the period of March 2008 to April 2009.

Most noticeable was the occurrence of several rather short periods with a drop in air temperature and also solar radiation, combined with high wind velocities, especially at the beginning of March, July, and August and between 18.11.08 and 26.11.08.

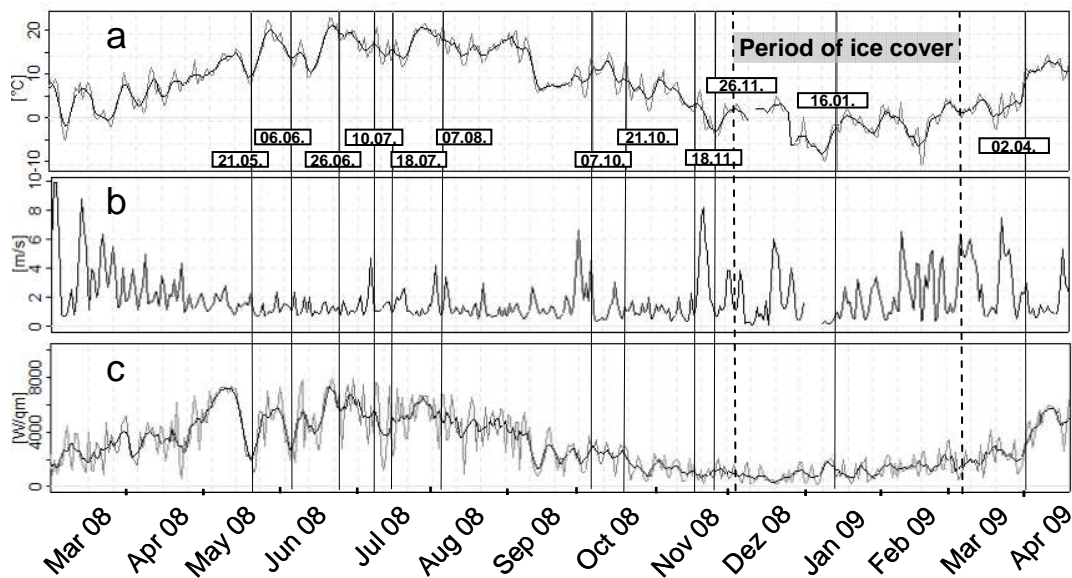


figure 6: weather data in the study area for the investigated period from March 2008 to April 2009. a. daily mean of air temperature [$^{\circ}\text{C}$] (thin line) with the 5d running mean (bold line) b. mean daily wind speed [ms^{-1}] c. daily sum of solar radiation [Wm^{-2}] (thin line) with the 5d running mean (bold line). Water $\delta^{18}\text{O}$ samplings are indicated by vertical lines and the respective date.

3.4.2 Development of water temperature and Schmidt stability

The progression of lake water temperatures from March 2008 to April 2009 is depicted in Figure 7. a, c, e, and the calculated Schmidt stability S values in Figure 8.

In Lake Waschsee, summer water warming was considerably dampened and visible over the whole depth, which resulted in very low Schmidt stability values (max. $11.3 \text{ g cm cm}^{-2}$).

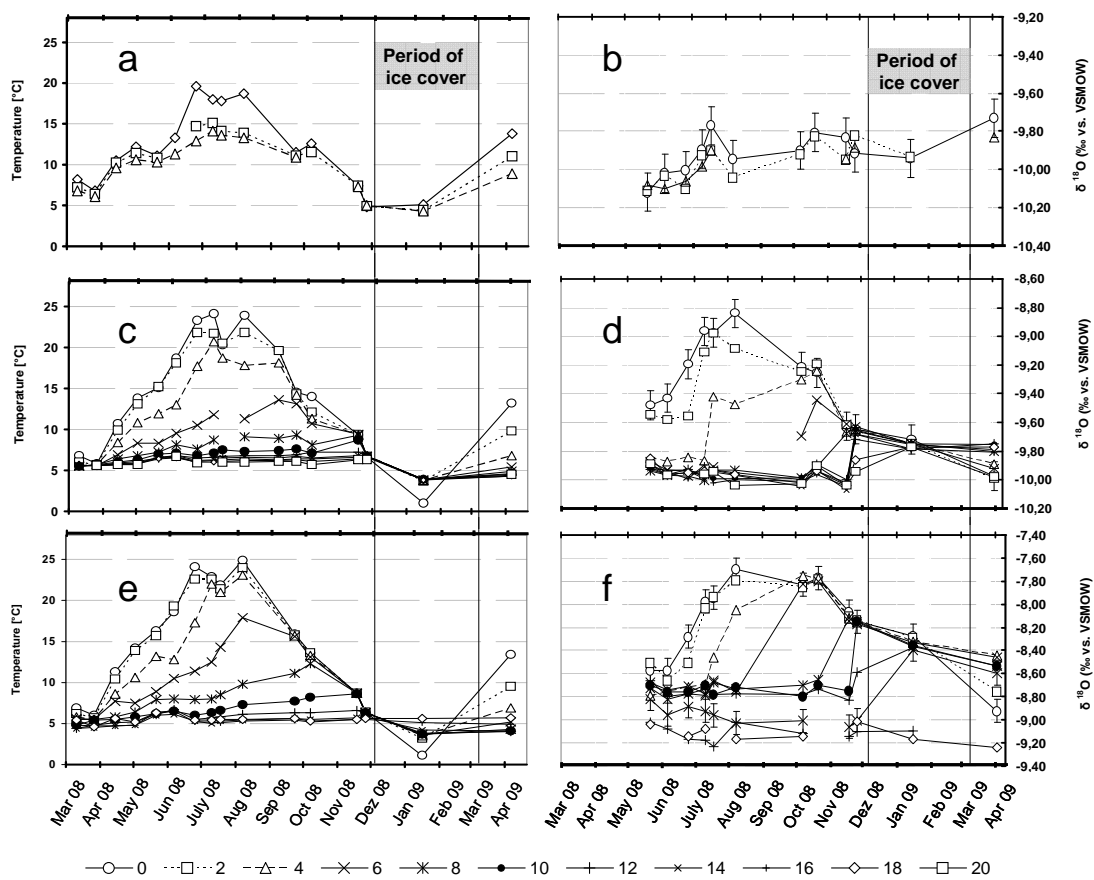


Figure 7: Development of water temperature [°C] (left side) and oxygen isotopic signature $\delta^{18}\text{O}$ [‰] from March 2008 to Apr 2009 (right side) in the investigated lakes (a, b: L. Waschsee, c, d: L. Fohnsee, e, f: L. Eishaussee).

In the middle of the summer stratification period Lakes Fohnsee and Eishaussee showed an episode of considerable cooling (26.06.08 – 18.07.08) in the course of which surface waters to a depth of 4 m became isothermal. This resulted in a significant drop of the stability reached earlier (up to 25% in Lake Fohnsee). After this clear break the upper water layers were again subjected to substantial warming in late summer (07.08.08) and therefore exhibited high stability values (Lake Fohnsee: 502 g cm cm^{-2}). The end of the thermal stratification and the slow erosion of the

epilimnion set in after 07.08.08 with the autumnal cooling of the lakes, which resulted in a continuous decline of Schmidt stability. Successive cooling led to a downward extension of the isothermal zone visible in the following samplings, so that on 26.11.08 after a strong storm event all lakes were in an isothermal state. About one week later, the formation of ice set in on Lakes Fohnsee and Eishaussee and rendered them continuously covered with ice until the middle of March 2009.

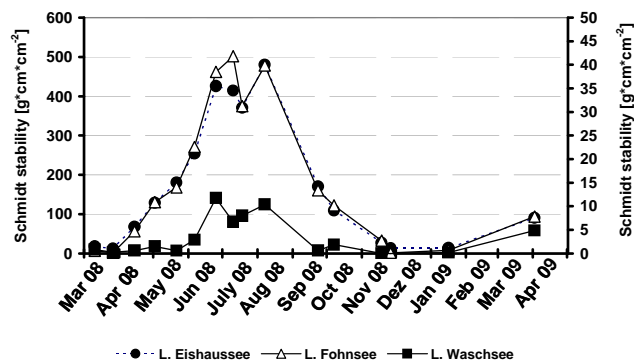


Figure 8: Development of Schmidt stability [g cm cm⁻²] from March 2008 to April 2009 in the investigated lakes. Note the different scales used for Lakes Fohnsee und Eishaussee (left) and L. Waschsee (right)

3.4.3 Development of ¹⁸O isotopic signatures

The overall development of $\delta^{18}\text{O}$ in the water column was similar in Lakes Fohnsee and Eishaussee (Figure 7d, f). $\delta^{18}\text{O}$ of upper water layers steadily increased during summer months (May – August 2008) and returned to more depleted values in late autumn (August – November 2008). While in Lake Fohnsee this depletion led to a uniform isotope signal across the entire water column on 16.01.09, in Lake Eishaussee this homogenisation of $\delta^{18}\text{O}$ was constrained to a depth of 0 m – 14 m. The bottom water layers (16 m, 18 m) remained significantly ($p < 0.001$) separated in signal from upper layers over the whole period of investigation.

In Lakes Fohnsee and Eishaussee the influence of isotopic enrichment during summer was only visible in the topmost water layers (0 m, 2 m), but began to extend to a depth of 4 m from 18.07.08 on. In autumn, a combination of two processes led to a uniform isotopic value in January 2009, being either restricted to parts of the water column (Eishaussee) or comprising all water layers (Fohnsee): First, a decline in signal extending from the water surface and secondly, several quite sudden increases of $\delta^{18}\text{O}$ in bottom water layers up to the current lake surface $\delta^{18}\text{O}$ value. Both absolute values of $\delta^{18}\text{O}$ and signal ranges proved to be different for the

investigated lakes: In Lake Waschsee (Figure 7b), the overall range of oxygen isotope signatures was rather narrow ($\Delta \delta^{18}\text{O} = 0.38\text{‰}$) and the mean isotopic value ($\delta^{18}\text{O} = -9.94\text{‰}$) of all water layers over the investigated period was closer to the signature of local groundwater ($\delta^{18}\text{O} = -10.01\text{‰} \pm 0.06\text{‰}$) than the respective mean values of the other lakes. In Lake Waschsee isotopic differences between water layers were always below or close to analytical precision, although in the surface water layer a trend towards stronger isotopic enrichment and therefore a separation in signal from lower layers was apparent from 06.06.08 to 07.10.08. The respective mean isotopic values of the whole lake at the beginning (21.05.08) and at the end (02.04.09) of the sampling campaign were markedly different ($\delta^{18}\text{O} = -10.12\text{‰} / -9.75\text{‰}$).

This did not apply for Lakes Fohnsee and Eishaussee (Figure 7 d, f), where differences between the mean isotopic values of the water column on the first (21.05.08) and the last (02.04.09) sampling were only minor ($\Delta\delta^{18}\text{O} = 0.11\text{‰}$, 0.03‰). However, in the course of the study $\delta^{18}\text{O}$ values exhibited pronounced variation ($\Delta\delta^{18}\text{O} = 1.20\text{‰}$, 1.23‰) and the mean isotope value of all water layers was higher ($\delta^{18}\text{O} = -9.66\text{‰}$, -8.41‰) than in Lake Waschsee.

At the last sampling, conducted several days after ice melt, surface water layers to a depth of 4m were characterised by lower oxygen isotopic values than the water layers below, although the difference ($\Delta\delta^{18}\text{O} = 0.16\text{‰}$) was close to analytical precision. This could also be seen in the surface layers (0m, 2m) of Lake Eishaussee (0.32‰).

Interestingly, the hypolimnion (10 - 20m depth) in Lake Fohnsee showed a highly significant trend ($n = 47$, $r^2 = 0.65$, $p < 0.001$) towards lower oxygen isotope values from the beginning of the sampling campaign to the last day of stratification (21.05.08 - 18.11.08, without 21.10.08).

3.5 Discussion

3.5.1 Local weather

The periods around 21.05.08 and 17.06.08 with a substantial drop in air temperature and solar radiation, but low wind speed affected the rising trend of water temperatures and stability only slightly.

In contrast to this, in July a period with comparatively small drops in air temperature and solar radiation had a strong effect on Schmidt stability, surface water temperature and isotopic signature. This is possibly due to the fact that after a long rather calm period a short event of strong wind occurred around 08.07.08, which is likely to have induced high shear velocities on the lakes surface, therefore enforcing the cooling of upper water layers and the deepening of the epilimnion, as seen in the isotopic signatures of the respective water layers. For Lake Eishaussee this might as well apply to the next wind event around 04.08.08, although in the meantime a considerable rise in air temperature occurred.

The autumnal cooling period began with a pronounced drop of air temperature in the middle of September (14.09.08) and was accompanied by two strong wind events (01.10.08 / 21.11.08), the latter coinciding with air temperatures below 0° C and followed by an isothermal situation in all three lakes.

3.5.2 Development of water temperature, stability and $\delta^{18}\text{O}$

Lake Waschsee

The relatively small observed range of both water temperature and $\delta^{18}\text{O}$ is a result of the very high water renewal rate, which is due to the low total volume and a strong subsurface inflow of groundwater with a uniform temperature of ca. 9°C (Melzer 1976). Besides the incomplete formation of an ice cover, the strength of this influence is also evident since the mean $\delta^{18}\text{O}$ signal of all water layers always remained closer to the signature of local groundwater than it was observed in the other lakes. The overall Schmidt stability was about 40 times lower than in Lakes Fohnsee and Eishaussee and is in the same range as reported for other polymictic small lakes, e.g. Lake Marion near Vancouver BC, Canada, (11g cm cm⁻²) with a water renewal rate of approximately 76 times per year (Kjensmo 1994). The polymictic character of Lake Waschsee was more evident in the isotopic signature than in temperature profiles: While the surface (0m) temperature showed considerable separation (up to

5°C) from the remaining water body between 21.05. – 07.10.08, the isotopic signal of bottom water layers clearly followed the surface water $\delta^{18}\text{O}$ trend and isotopic differences between these layers were always minor.

Although seeming contradictory at first, this might be due to the fact that the surface water temperature usually reflects a daily pattern, while the isotope signal integrates over time. Near-surface thermoclines that form and disappear in a diurnal rhythm are a very common phenomenon in small, wind protected lakes (Imberger 1985, Xenopoulos & Schindler 2001). The pronounced differences in the mean $\delta^{18}\text{O}$ of Lake Waschsee at the beginning and end of the sampling campaign are consistent with the explanation presented by Gibson *et al.* (2002) that lakes of smaller volume and water residence time below one year are likely to show a seasonally fluctuating mean isotopic signature. Lakes of larger volume, higher water residence time and therefore a large buffer capacity for water $\delta^{18}\text{O}$ are expected to exhibit near-constant signals, as they were shown for Lakes Fohnsee and Eishaussee.

Lake Fohnsee

As in the case of Lake Waschsee, in Lake Fohnsee the $\delta^{18}\text{O}$ signal was a better indicator of the state of isolation and mixing of water layers than their respective temperature. While during most of the early summer (26.03.08 – 06.06.08), the upper two water layers remained virtually indistinguishable in temperature, the isotopic signature in 2 m depth remained unaffected by the continuous enrichment in the topmost layer until 26.06.08. In the following, the drop in air temperature resulted in a cooling of surface waters and a corresponding drop in Schmidt stability, which increased the susceptibility for wind-induced mixing. The storm event at 08.07.08 produced an erosion of the thermocline and a deepening of the epilimnion by entrainment as indicated by the sudden leaps of $\delta^{18}\text{O}$. Visible in the stable $\delta^{18}\text{O}$ isotopic signature but not in the temperature profile, the effect of this entrainment had extended to the depth of 4m at the following sampling.

Entrainment during the stratification period can be a determining factor for the intensity of primary production and algal blooms, as nutrients are released from the hypolimnion into the euphotic zone: Soranno *et al.* 1997 investigated the epilimnetic Phosphorus budget of a North American eutrophic lake and found the amount of Phosphorus transported to the Epilimnion by Entrainment to exceed external loading by an order of magnitude in one year.

The windy but warm period at the beginning of August did not affect the separation of the surface layers (0m , 2m) as indicated by both $\delta^{18}\text{O}$ and temperature. The marked decrease of $\delta^{18}\text{O}$ originating from the surface layers in autumn and early winter is the result of a combination of several effects. First, the influence of evaporation enrichment was lifted; therefore the evaporation / inflow ratio decreased and the $\delta^{18}\text{O}$ signal of the inflow became more determining (Gibson *et al.* 2002). Secondly, precipitation (rainfall and surface runoff) typically displays lower isotope signatures and precipitation levels increase in autumn and winter compared to summer (Mook & Rozanski 2000). This is confirmed for the investigated area by the long term weighted means for $\delta^{18}\text{O}$ of precipitation in August (-7.96 ‰) and October (-12.35‰) at the nearest GNIP station of Hohenpeissenberg (<http://nds121.iaea.org/wiser/>).

The abrupt rises in $\delta^{18}\text{O}$ of single bottom water layers visible in autumn are likely due to stepwise entrainment of those layers and mixing with surface water. The isotopic signature revealed for Lake Fohnsee and the upper dimictic part of Lake Eishaussee that the isothermal state on 26.11.08 after a strong storm event did not coincide with a circulation of the whole water column. Full homogenisation of $\delta^{18}\text{O}$ was not visible until 16.01.09 when sampling was conducted under ice. This implicates further mixing either prior to or after the formation of ice. The latter is supported by additional evidence, as the sampling under ice did not reveal a different isotopic signature of the surface water layer, as would otherwise be expected. During the formation of ice out of liquid water preferentially heavy isotopes are incorporated into the solid state (Friedman and Redfield 1957 cit. in Tyler *et al.* 2007). Therefore the surface water directly beneath the ice is expected to be, at least to some degree, depleted of heavy isotopes compared to the remaining water column. This effect has been shown to be significant for $\delta^{18}\text{O}$ even in the whole water column of antarctic and alpine lakes (Krabbenhoft *et al.* 1990, Gibson *et al.* 2002). Some disturbance of water layering might have been induced during the removal of the ice for sampling. However, we suggest that the absence of a different surface water $\delta^{18}\text{O}$ and the clear trend towards more depleted isotopic signatures visible in all water layers of Lake Fohnsee and the mixolimnion of Lake Eishaussee are a sign of ongoing mixing processes under the ice layer. This phenomenon was also frequently reported for ice covered lakes by other authors (Farmer 1975, Bengtsson 1996, Petrov *et al.* 2007).

At the last sampling on 06.04.09 the onset of snow and ice melt was clearly reflected by depleted ^{18}O surface water signals (cf. Mook & Rozanski 2000). Accordingly, the significantly lower isotope signature of the bottom water layer (20 m) at this sampling ($\delta^{18}\text{O} = -9.98 \text{ ‰}$) might be due to the influence of melt water sinking to the bottom of the lake as described by Tyler *et al.* (2007) for a small Scottish lake. However, the reason for this remains unclear, as the almost uniform temperature of bottom waters was close to the point of maximum density.

The highly significant trend towards more depleted oxygen isotope values which was visible in the bottom water layers of Lake Fohnsee indicates considerable groundwater inflow during the study period, as the isotopic signature of water can only be changed via significant mass transport (Dinçer 1968). This is an important finding, because until now, Lake Fohnsee had not been considered receiving significant groundwater inflow (Melzer 1976). Since we are not able to give a concise explanation for the rise of $\delta^{18}\text{O}$ visible in all bottom water layers of Lake Fohnsee on 21.10.08, the isotopic results of this sampling were not used in the calculation of the regression.

Lake Eishaussee

Under given climatic conditions, the mean oxygen isotopic composition of a lake is determined only by the long term means of both the isotopic composition of the inflow and the ratio of inflow / evaporation (Dinçer 1968, Gibson *et al.* 2002). Lake Eishaussee is considered not to be influenced by groundwater (Melzer 1976) and receives its inflow from surface water layers of the neighbouring lakes. This permits a considerable isotopic enrichment of its inflow compared to the original groundwater by the “string-of-lakes” effect as described by Gat & Bowser (1991). However, one of the lakes connected to Lake Eishaussee is Lake Fohnsee with a mean isotopic signature quite close to $\delta^{18}\text{O}$ of local groundwater. Therefore we propose that the relatively depleted mean oxygen isotopic signal found in Lake Eishaussee is the result of a water residence time significantly higher than in Lake Fohnsee, as both are subjected to the same climatic conditions. In Lake Fohnsee, the possible effect of isotopic enrichment by evaporation is likely to be attenuated by dilution (Gibson *et al.* 1996) due to a higher water renewal rate and inflow of isotopically depleted groundwater.

The permanent meromictic situation of Lake Eishaussee was clearly reflected by the continuous separation in $\delta^{18}\text{O}$ of the monimolimnion (16m, 18m) from the mixolimnion during the whole study period. The oldest published record mentioning this condition of Lake Eishaussee (Zorell 1941) allows the conclusion that the lake has been meromictic for the last 70 years. Recent sediment investigations in Lake Eishaussee indicate that it has been meromictic for much longer (Braig, to be published). The sampling under ice on 16.01.08 revealed a full circulation of water layers from 0 – 14 m depth, which was not present at the sampling at isothermal conditions before. Thus, the $\delta^{18}\text{O}$ signal indicates that the boundary between mixolimnion and monimolimnion is somewhere between 14 m and 16 m depth, which is confirmed from conductance depth profiles (data not shown).

The location of Lake Eishaussee is protected against wind influences considerably more than that of the other investigated lakes. While this condition may have helped in the conservation of the present meromictic situation, it was noticeable to a small amount in the isotopic signature of the surface water layers (0m, 2m): They repeatedly showed different oxygen isotopic signatures over the summer, although this effect was almost always below analytical precision.

3.6 Conclusions

The extent of stratification and mixis especially during the summer stratification is a determining aspect for the vast majority of lakes in temperate regions of low to mid altitude, as it is bound to have important effects on nearly all biological, chemical and physical processes, especially on the trophic state and primary production. However, though being crucial, the occurrence of mixing events in the water column is not always easily detected by standard measurements.

The present study of $\delta^{18}\text{O}$ in the water column of three lakes with very different hydrology proved the high suitability of the stable oxygen isotopic signature of water for the routine investigation of important mixis and stratification processes in lakes.

The presented findings confirm important implications for lake water balance investigations that use the degree of isotopic enrichment in a water body to account for the influence of evaporation compared to inflow (Gibson *et al.* 1996, Mayr *et al.* 2007, Yi *et al.* 2008). As already pointed out by Gibson *et al.* (2002), the influence of evaporation is easily overestimated when the assumption of an isotopically well mixed reservoir is not valid and a stronger enrichment is found in the sampled

topmost water layers. Depending on the desired level of precision, sampling should thus cover the whole water column with suitable temporal resolution to account for such influences.

This should also be considered an important implication for paleoclimatic studies that use the oxygen or hydrogen isotopic signal of authigenic or biogenic components (e.g. diatoms, chironomids, authigenic and biogenic carbonates) produced in certain depths and seasons, to reconstruct past lake water $\delta^{18}\text{O}$ (e.g. Wooller *et al.* 2004, Leng & Barker 2006, Wolfe *et al.* 2007). The input functions for these materials need to be carefully defined, as the seasonal and spatial variations revealed by our study are likely to induce considerable non-systematic error to such reconstructions of lake water $\delta^{18}\text{O}$.

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4 Fifty years of eutrophication and lake restoration reflected in sedimentary carbon and nitrogen isotopes of a small, hardwater lake (South Germany)

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Running title: 50 years of eutrophication and lake restoration reflected in sedimentary isotopes

4.1 Abstract

This study analyses the response of the carbon and nitrogen isotopic composition of sedimentary organic matter to rapid human-induced eutrophication and meromixis as well as subsequent restoration efforts (in-lake Phosphorus (P)-Precipitation, P-remediation of the well inflow and multiannual destratification) in a 46-yr sediment core sequence (1963 – 2009) from Fischkaltersee, a small hard-water lake (S-Germany). In addition, the sediment record was compared with detailed data on water column chemistry during almost (1977 - 2009) the recorded history of eutrophication and trophic recovery of the named lake.

While the onset of eutrophication resulted in an abrupt positive excursion (+2.4 ‰), the overall reaction of $\delta^{13}\text{C}_{\text{SOM}}$ to ongoing eutrophication and meromixis as well as to permanent hypolimnion aeration and trophic recovery is a continuous negative trend (-3.7 ‰) with the most depleted signatures (-38.8 ‰) present in the youngest part of the core. This negative trend was not influenced by multiannual hypolimnion aeration, which although oxygenating bottom waters ($> 2 \text{ mg O}_2 \text{ L}^{-1}$), did not reverse the increasing anoxia in the sediment, as is indicated by an declining Mn/Fe ratio. Hence, we conclude that in Fischkaltersee $\delta^{13}\text{C}_{\text{SOM}}$ was controlled by photoautotrophic input only during an early phase in the eutrophication process. According to the conceptual model of Smith and Hollander 2001, the signal of intensifying microbially mediated carbon cycling processes in the sediment, i.e. methanogenesis and methanotrophy, was superimposed on the primary productivity signal by crossing a certain TP threshold (approx. $\text{TP} = 0.04 \text{ mg L}^{-1}$)

Sedimentary $\delta^{15}\text{N}$ values exhibit an overall increase (+3.4 ‰) in reaction to the eutrophication process, while trophic recovery produces a continuous decrease in the signal (-2.7 ‰)

Linear correlation of $\delta^{15}\text{N}$ to nitrate utilisation in the epilimnion, however, is rather weak ($R^2 = 0.33$). Comparison between sediment $\delta^{15}\text{N}$ values and water column data reveals that two negative shifts in the isotopic signal (-1 ‰ / -0.6 ‰) around 1980 and 1984 respectively, can be attributed to the existence of significant amounts of ammonium (up to 2 mg L^{-1}) in the trophogenic zone. Coincident drops in nitrate utilisation (-20 % / -53 %) indicate phytoplankton assimilation of ammonium. As the artificial aeration did also not affect $\delta^{15}\text{N}$, we conclude that water column denitrification never contributed significantly to the sedimentary N isotope signal.

4.2 Introduction

Investigations of the carbon as well as the nitrogen isotopic composition of autochthonous organic matter have become standard tools for the reconstruction of lacustrine paleoproductivity (Hodell and Schelske 1998, Brenner et al. 1999, Meyers 2006, Drew et al. 2008) as the combined analysis of the stable isotopes of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) of sediment organic matter (SOM) also offers the potential to identify organic matter (OM) sources (Mayr et al. 2005) or to reconstruct changes in the nutrient cycling (Heyng et al. 2012). Phytoplankton preferentially incorporates the lighter carbon isotope ^{12}C during assimilation (Farquhar et al. 1989). The resulting enrichment of ^{13}C in the dissolved inorganic carbon (DIC) pool in the surface water is proportional to the intensity of primary productivity. It is recorded in the biomass produced and deposited in the sediment thereafter (Teranes and Bernasconi 2005). Primary productivity can be the dominant control of $\delta^{13}\text{C}_{\text{SOM}}$, therefore the latter has been widely used as a proxy indicator of eutrophication processes (McKenzie 1985; Hollander and McKenzie 1991; Brenner et al. 1999).

Marine studies (Sigman et al. 1999) revealed a strong relationship between the $\delta^{15}\text{N}$ values of SOM and the degree of surface water nitrate (NO_3^-) utilisation (and therefore the intensity of primary productivity as well). This correlation seems to be somewhat weaker in lacustrine environments, as here the factor limiting primary productivity often is phosphorus rather than nitrogen (Wetzel 2001), thus a sufficient consumption of the surface water N pool is the exception. When only a minor part of the dissolved inorganic nitrogen (DIN) pool of the surface water is consumed, its N isotopic composition will remain largely unaltered and an intensifying primary production will not be reflected in a corresponding increase in $\delta^{15}\text{N}_{\text{SOM}}$ (Teranes and Bernasconi 2000)

Nevertheless, several studies proved the significance of a primary productivity effect on $\delta^{15}\text{N}_{\text{SOM}}$ in lacustrine environments (Teranes and Bernasconi 2000, Talbot 2001).

However, the interpretation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM in terms of paleoproductivity can be complicated by a variety of processes in the rather complex lacustrine C- and N-cycles that can also have a strong impact on the C and N stable isotope ratios of SOM but are not necessarily correlated to the intensity of primary productivity.

Antropogenically induced eutrophication often produces anaerobic conditions in the bottom waters and in the sediment which promote the intensification of

microbially mediated processes. For instance, the formation (methanogenesis) and oxidation (methanotrophy) of methane as well as denitrification have the potential to impart strong changes in the isotopic signal of $\delta^{13}\text{C}_{\text{SOM}}$ and $\delta^{15}\text{N}_{\text{SOM}}$, respectively (Finlay and Kendall 2007), as the isotope fractionation effects associated with these processes are pronounced.

This is obvious for microbial methane (-110 ‰ to -50 ‰, Whiticar 1999), which is produced in enormous amounts in strictly anoxic zones of the water column or sediment (Nitzsche et al. 2009). Subsequently, a large part of this methane can be oxidized in the overlying oxic water layers, and thus be re-integrated into the epilimnetic DIC pool.

As well, the microbial biomass itself can have a significant effect on the carbon isotopic signature of SOM, as bacterial OM and its metabolites are strongly depleted in ^{13}C (Whiticar 1999).

Denitrification on the other hand, which is also a bacterially mediated process and essentially dependent on anoxic conditions, produces considerable enrichment of ^{15}N in the remaining DIN pool, as during the reduction of nitrate NO_3^- to nitrous oxide NO_2 and dinitrogen N_2 , the forms of nitrogen bearing the lighter isotope ^{14}N are consumed more rapidly. In marine studies, the associated isotope effects ranged between +20‰ to +30‰ (Granger et al. 2008). Thus, dependent on the extent of anoxia in a lake, denitrification can be an important influence on $\delta^{15}\text{N}_{\text{SOM}}$, thus masking the effect of primary productivity.

Moreover, it is well known that the isotopic composition of the DIN pool can be significantly altered by the signal of external N loading to the lake, which is especially true for anthropogenically eutrophicated systems, as sewage and agricultural runoff can be considerably enriched in $\delta^{15}\text{N}$ (Talbot 2001).

Considering these processes, detailed knowledge about the biogeochemical conditions in the water column during the entire process of eutrophication is essential for studies of paleoproductivity based on $\delta^{13}\text{C}_{\text{SOM}}$ and $\delta^{15}\text{N}_{\text{SOM}}$. In many cases such information is not available or has to be inferred from other proxy indicators, which can lead to inappropriate conclusions.

Therefore, field studies are needed to test the possible impact of these processes on $\delta^{13}\text{C}_{\text{SOM}}$ and $\delta^{15}\text{N}_{\text{SOM}}$ by comparing detailed water column data with the sediment record produced during the same time period, which ideally should consist of all

stages of anthropogenically induced eutrophication and also trophic recovery of a lake.

As complete records containing both detailed sediment and water column data of the eutrophication process of a single lake are rare, this can also be achieved by applying a space-for-time approach, where recent sediment depositions of different lakes spanning a broad range of trophic stages are compared (Woodward et al. 2012).

In this study, we report on the effect of a period (ca. 46a) of severe eutrophication as well as subsequent restoration measures on the sedimentary isotope signatures $\delta^{13}\text{C}_{\text{SOM}}$ and $\delta^{15}\text{N}_{\text{SOM}}$ in Fischkaltersee, a small pre-Alpine hardwater lake in Bavaria, Southern Germany. The main advantage of the site is the detailed knowledge about the lake chemistry during the various highly invasive restoration approaches. The latter were initiated in reaction to the rather fast anthropogenically induced eutrophication of Fischkaltersee and consisted of chemical P-precipitation, followed by multiannual permanent and afterwards a period of intermittent destratification. Thus we are able to examine the effects of these lake restoration attempts in great detail both for the water column as well as for the sediment. This study might also be of relevance for the interpretation of sedimentary isotope values in terms of natural eutrophication.

4.3 Methods

4.3.1 Site description

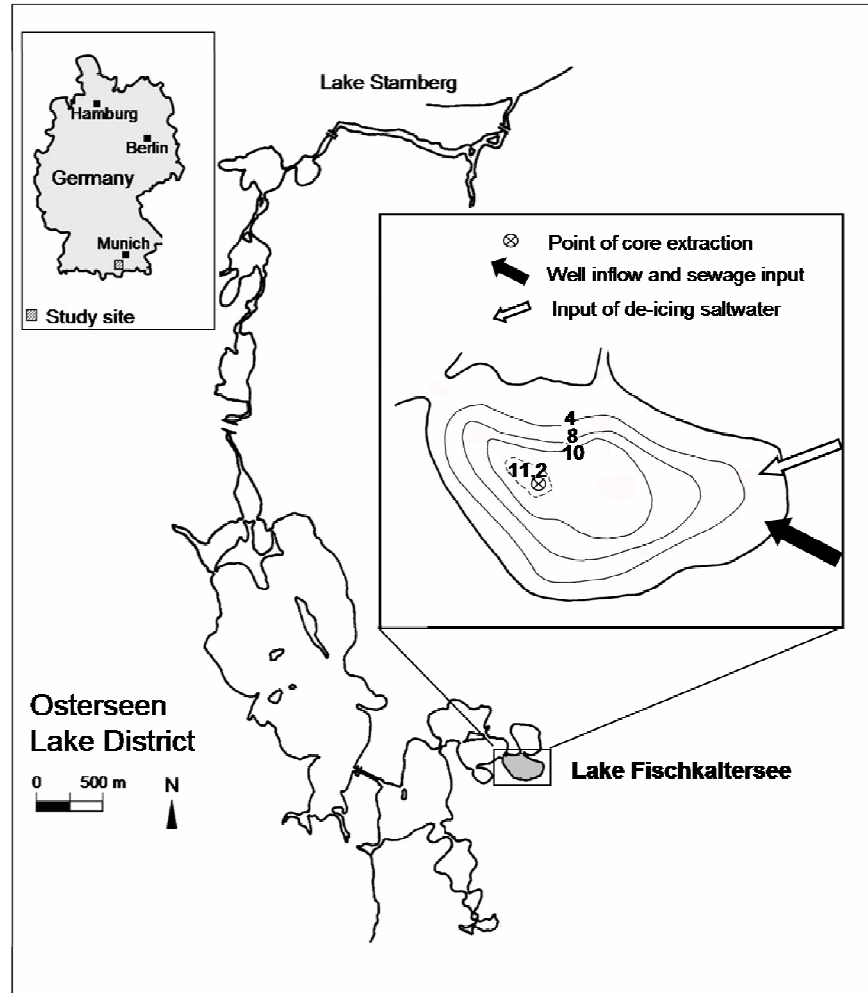


Figure 9: Outline map of the geographic location of the Osterseen Lake District and the position of the investigated lake, Fischkaltersee (grey filling). The bathymetric map shows the point of core extraction and the inflows of well water, sewage and de-icing saltwater to Fischkaltersee.

Fischkaltersee (47°46'52.54" N, 11°19'21.00" W) is a small head lake of a side chain of the pre-Alpine lake district Osterseen located in Bavaria, Southern Germany (Figure 9). Morphometric characteristics of Fischkaltersee are given in Table 3. The main surface inflow to the carbonate-rich kettle lake is an adjacent surface groundwater well with a mean delivery rate of ca. 5 L s⁻¹ (Steinberg and Niesslbeck 1981).

Runoff from an agricultural area and increasing local sewage disposal in the nearby village of Staltach which both drained to the catchment of the well (Steinberg and Zimmermann 1988) resulted in an rapid increase in trophic level starting in 1970

(Melzer 1976, Steinberg and Fischer 1982). However, ongoing investigations of a neighbouring lake in the side chain indicate that the original trophic state of those lakes might have been already altered by the mid of the 20th century (Braig, unpublished results).

Table 3: Morphometric and hydrologic data of Lake Fischkaltersee

Surface area	0.034 km ²
Max. depth	11.2 m
Mean depth	5.7 m
Volume	1.8 x 10 ⁵ m ³
Drainage area	0.3 km ³
Theoretical water retention time	143 d

In 1974, when the concentration of Total Phosphorus (TP) in the well water was 279 µg L⁻¹, Fischkaltersee had already become eutrophic with TP = 40 µg L⁻¹ and an periodically anaerobic hypolimnion (Melzer 1976, OECD 1982), but remained dimictic until 1975. From 1974 on (Steinberg and Fischer 1982), the lake was also loaded with considerable amounts of salty water from a nearby street junction during annual snowmelt (up to 200 mg Cl⁻ L⁻¹, Steinberg and Zimmermann 1988). This salt load increased the stability of bottom water stratification to the point of meromixis: depth profiles of conductivity taken during the routine measurements reveal a constant mean difference of 251 ±76 µS cm⁻¹ between bottom and surface waters until the onset of aeration. As a consequence, high concentrations of TP (2 mg L⁻¹), hydrogen sulfide H₂S (15 mg L⁻¹) and ammonium NH₄⁺-N (22 mg L⁻¹) were measured in the anoxic monimolimnion of Fischkaltersee in 1979. By then, the TP input from the well had increased considerably to 450 µg L⁻¹ (Steinberg and Bucksteeg 1980) and remained high for most of the period of the following lake restoration program, as Staltach was not connected to a centralized sewage plant until 1981 (Steinberg and Zimmermann 1988). In addition, considerable P-desorption from the saturated aquifer occurred afterwards (Steinberg and Zimmermann 1988), so that TP concentrations of >100 µg L⁻¹ in the trophogenic zone rendered the lake hypertrophic (OECD 1982).

These circumstances gave reason to a scientifically motivated lake restoration program conducted and monitored by the State Office for Water Management of Munich (Steinberg and Bucksteeg 1980). The program consisted of routine

monitoring of water column parameters as well as highly invasive remediation measures.

While sporadic water column data have been available since 1974, routine measurement of physical and chemical water column parameters began in 1977 and was conducted biweekly until 1993 and bimonthly until 2000. From then on, measurements were only conducted in 2005 and 2008.

Remediation measures began in late December of 1979 with a phosphorus precipitation measure: Overall, 14 tons of aluminium hydroxide ((Al₂(OH)_{3.36}Cl_{2.13}(SO₄)_{0.25} Steinberg and Bucksteeg 1980) were pumped into different depths of the lake on two consecutive days, producing a continuous, 10 to 70 mm thick layer of aluminium-hydroxide-P-complex (alumn, Wauer 2006) over the entire lake sediment (Steinberg and Bucksteeg 1980, Steinberg and Fischer 1982). At first, this measure seemed to be successful, as the concentration of TP was reduced by more than 50 % in the trophogenic zone immediately after the restoration measure (Steinberg and Bucksteeg 1980). Furthermore, the biomass of the phytoplankton was reduced by 90 % via coprecipitation. But only a few weeks after the treatment TP concentrations in the trophogenic zone rose to 50 µg L⁻¹ and polytrophic phytoplankton communities developed again. To fight the algal blooms and to establish oxic, P-retaining conditions at the sediment-water interface, a system of hypolimnetic aeration was established for permanent destratification of Fischkaltersee, starting in May 1980. However, this treatment was not effective, as it resulted in a doubling of viable biomass of primary producers, a fivefold increase in plate counts of heterotrophs and also common oxygen depletion at the sediment-water interface (Steinberg and Schrimpf 1982). The permanent destratification was maintained until 1984 and changed into an intermittent mode from 1985 onwards, as problems with phytoplankton blooms continued. In conjunction with P-restoration of the well inflow, a rhythm of 21 days of aeration followed by a break of one week, led to a continuous decrease in both TP and biomass concentrations (Steinberg and Zimmermann 1988), so that from 1993 until 2000, aeration was only performed in spring and autumn to support natural circulation (pers. commun. B.B. 2010). After 2000, all remediation measures were stopped. Today, Fischkaltersee is in a mesotrophic, dimictic state with TP = 29 µg L⁻¹ (pers. commun. B.B. 2010).

4.3.2 Field and laboratory Methods

In August 2009, a 48 cm long gravity core (FIS 8/09) was recovered from the western section of the deepest basin of Fischkaltersee (Figure 9 and 10) using an UWITEC gravity corer.

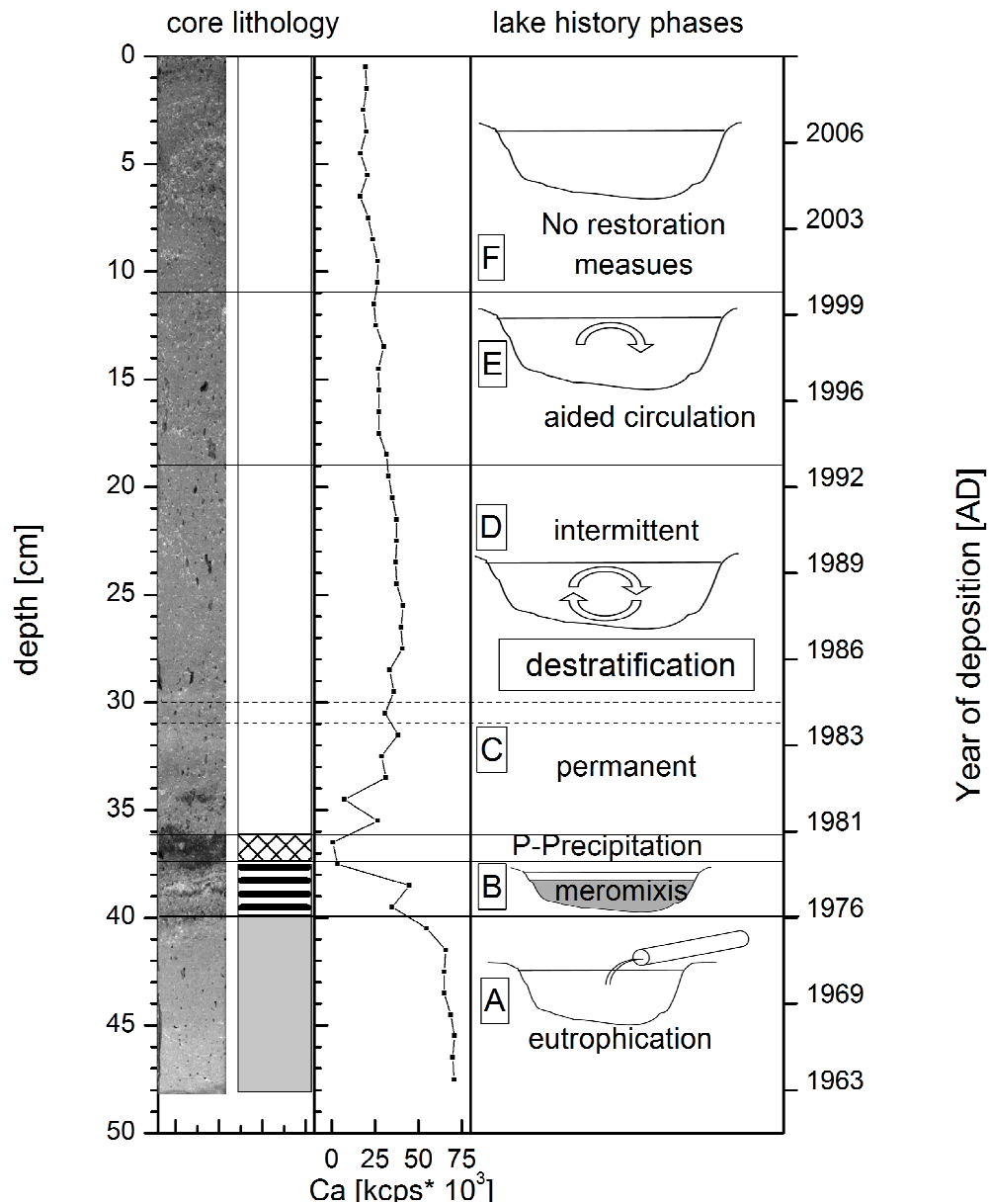


Figure 10: Photograph of half-core surface, core lithology (left panel) and depth profile of XRF-derived Ca counts (middle panel, indicated as kilocounts per second) of core FIS 8/09. The right panel shows the corresponding phases of lake history and the years of sediment layer deposition, according to the age-depth model.

The core was stored at 4°C in the dark until further processing. In the laboratory, the core was split lengthwise in two halves that were photographed and described lithologically. Non-destructive X-ray fluorescence (XRF) scanning (Mo tube, 200-µm

step size) of one split-core surface was carried out at 0.2 mm resolution with an ITRAX XRF core scanner (Cox Analytics, Sweden) (Lüder et al. 2006, Croudace et al. 2006). After XRF analysis, both halves of the core were sampled continuously and volumetrically in slices of 1 cm. The resulting subsamples were weighed and freeze-dried for determination of dry density and water content. Macroscopic remains of terrestrial plants were removed prior to further analyses. Subsamples of one core half were used for determination of ^{210}Pb and ^{137}Cs activity concentrations (Nehyba et al. 2011). Briefly, a γ -ray spectrometer equipped with a high-purity Germanium well detector (Canberra, 36.6 % relative efficiency) was used to detect the activity concentrations of ^{210}Pb and ^{137}Cs . The activity of unsupported (excess) ^{210}Pb was calculated by subtracting ^{226}Ra activity, which is in equilibrium with the (supported) ^{210}Pb present in the sediment minerals, from total ^{210}Pb activity. Conventional dating models (Kirchner 2011) did not provide concise $^{210}\text{Pb}_{\text{excess}}$ sediment chronologies covering the entire core (see Section 4.4.1). Thus, ages were determined in a two-step approach as follows: First, linear interpolations between reference points of known deposition date (core surface, ^{137}Cs peaks, alumn layer) resulted in estimating mean time-invariant sedimentation rates. Second, the assumption of the rates being time-invariant was checked by fitting the Constant Initial Concentration (CIC) model (Krishnaswamy et al., 1971) to the unsupported ^{210}Pb concentrations between the individual time markers used for interpolation. Since the CIC model assumes that the sedimentation rate is constant, any systematic deviation with depth between measured predicted concentrations will indicate a time trend of the sedimentation rates, whereas mere scattering of measured excess ^{210}Pb around its predicted concentrations confirms that our assumption of a mean time-invariant sedimentation rate is reasonable.

Subsamples of the other core half were homogenized in a mortar prior to isotopic and elemental analysis. Prior to homogenization all macroscopic remains were removed. For determination of total nitrogen (%TN) and its isotope ratio R ($^{15}\text{N} / ^{14}\text{N}$), c. 8.0 mg of bulk sediment were weighed into tin capsules and combusted at 1080°C in an element analyzer (NC 2500, Carlo Erba, Italy) coupled to an isotope-ratio mass spectrometer (IRMS, DeltaPlus, Thermo-Finnigan). Prior to the analysis of total organic carbon content (%TOC) and its isotope ratio R ($^{13}\text{C} / ^{12}\text{C}$) in the IRMS, subsamples of c. 3.3 mg were weighed into silver cups and subsequently treated in situ with small (50 μl) amounts of 3 % hydrochloric acid (HCl) at 80°C to remove all

carbonate. This step was repeated until no further effervescence occurred. Then all samples were treated with 150 µl 20 % HCl and dried for 2h (Nieuwenhuize et al. 1994, Ryba and Burgess 2002, Kennedy et al. 2005).

Isotope ratios R are reported as per mill in the delta notation ($\delta^{13}\text{C}$ / $\delta^{15}\text{N}$) against the international reference standard VPDB (carbon) and AIR (nitrogen) respectively, where

$$\delta^{13}\text{C}_{\text{sample}}, \delta^{15}\text{N}_{\text{sample}} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000. \quad (4.1)$$

Precision derived from peptone standards analysed concurrently with samples is 0.10 ‰ (one standard deviation of > 65 standards) for both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$.

Comparisons using our own sediment standard showed good agreement between $\delta^{13}\text{C}_{\text{SOM}}$ of sediment (-33.40 ± 0.14 ‰) treated with this in situ carbonate removal and values produced with a rinsing procedure (-33.16 ± 0.15 ‰) (Mayr et al. 2005). We chose the in-situ method, as additional precaution had to be taken in removing all carbonate from this carbonate-rich (> 45 %) sediment samples. At such high carbonate concentrations, acid fumigation methods often fail to remove all inorganic carbon (Kennedy et al. 2005), which is essential for a reliable determination of $\delta^{13}\text{C}$ of SOM.

Unhomogenized subsamples from nine stratigraphic horizons were selected for diatom analysis using standard techniques (Battarbee et al. 2001). Briefly, 0.2 g of dry sediment sample were immersed in cold 30 % H_2O_2 for 12 h, followed by boiling in hot (80 – 100°C) H_2O_2 for 5 h and a final addition of potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ for complete oxidation of organic matter. For removal of carbonates, small drops of 30 % HCl were added to the remaining material. After cooling and pH-neutralisation, the diatom-rich residue was diluted, pipetted onto microscope coverslips and allowed to dry on a warming tray prior to mounting onto cover-slides with Naphrax. A minimum of 600 diatom valves was identified per sample at 1000x magnification using a Leica DM RBE microscope with DIC optics. Identifications were based on keys by Krammer and Lange-Bertalot (1986 -1991a,b). The diatom index (DI) as a reference system for trophic level and TP (Table 4) was calculated according to Hofmann (1993) and Schaumburg (2004). It has been developed and calibrated on several Bavarian lakes and is calculated from abundance and trophic preferences of the different taxa of benthic diatoms present in a sample, where

$$DI = \frac{\sum_{i=1}^n H_i \times G_i \times T_i}{\sum_{i=1}^n H_i \times G_i} \quad (4.2)$$

with H_i = relative abundance of taxon i , G_i = weighting factor for indicator quality of taxon i , T_i = trophic index of taxon i

Table 4: 2 Diatom index (Hofmann 1993) and ascribed trophic state vs. approx. TP corridors (OECD 1982)

Diatom index	trophic state	TP (OECD 1982)
1.00 – 1.99	oligotrophic	> 0.01 mg L ⁻¹
2.00 – 2.49	oligo - mesotrophic	
2.50 – 3.49	mesotrophic	0.01 – 0.035 mg L ⁻¹
3.50 – 3.99	meso – eutrophic	
4.00 – 5.00	eutrophic	0.035 – 0.1 mg L ⁻¹
Not defined	hypertrophic	> 0.1 mg L ⁻¹

From the comprehensive water column dataset produced during the lake restoration program, the following physical and chemical parameters were selected and are presented as four values per year where available:

TP, concentration of Chlorophyll a (Chl a), bottom water temperature ($T_{11\text{ m}}$), Oxygen content in 0 m and 11 m depth ($O_{2\ 0\text{m}, 11\text{m}}$), Nitrate-N concentration in 0 m and 11m depth ($NO_3^- \text{-N}_{0\text{m}, 11\text{m}}$), Ammonium-N concentration in 0 m and 11 m depth ($NH_4^+ \text{-N}_{0\text{m}, 11\text{m}}$).

TP and Chl a were calculated as a whole lake average applying a volume weighted function to the respective concentrations in the individual depths.

The degree of NO_3^- utilisation in the phototrophic zone NO_3^- utilisation was calculated as the relative depletion of $NO_3^- \text{-N}$ in 0 m depth within each annual productivity cycle (Lehmann et al. 2004)

$$NO_3^- \text{ utilisation} = \{1 - ([NO_3^- \text{-N}]_{\min} / [NO_3^- \text{-N}]_{\max})\} \times 100 \quad (4.3)$$

Dissolved Inorganic Nitrogen DIN-N was also calculated as a whole lake average sum of the concentrations of $NO_3^- \text{-N}$ and $NH_4^+ \text{-N}$.

All figures were produced with the program OriginPro 8.5 (OriginLab).

4.4 Results

4.4.1 Chronology

The chronology for FIS 8/09 based on activity concentrations ^{137}Cs and the alunn layer as a chronological mark is shown in Figure 11.

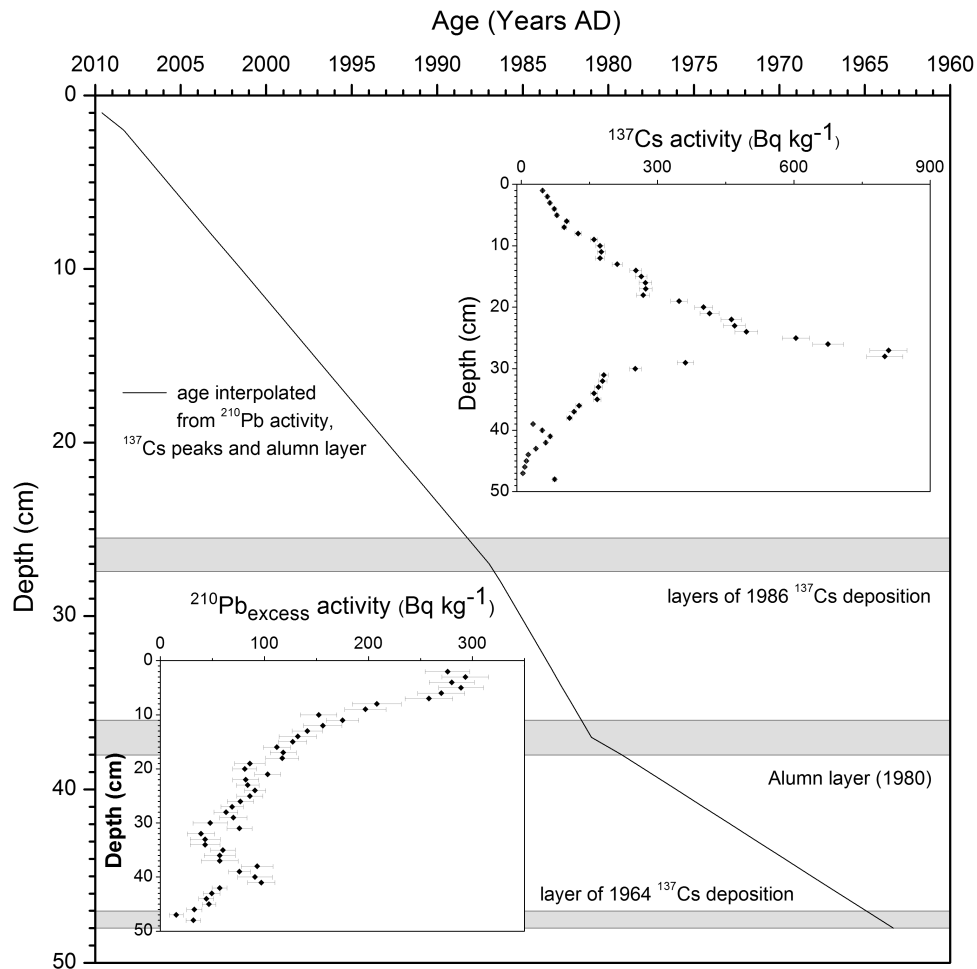


Figure 11: Age-depth model for core FIS 8/09 based on linear interpolation between reference points of known deposition date: core surface (0 - 1 cm, 2009), alunn layer (36 – 37.5 cm, 1980) and layers of ^{137}Cs deposition (47 – 48 cm, 1963; 26 – 27 cm; 1986). Detail graphs show the depth distribution of ^{137}Cs (above) and $^{210}\text{Pb}_{\text{excess}}$ (below) activity in the core FIS 8/09. Error bars indicate two standard deviations

First, a tentative core chronology was inferred from the ^{137}Cs tracer by linear interpolation between reference points of known deposition date, i.e. core surface, alunn layer and the two ^{137}Cs peaks in 1963 (weapons testing) and 1986 (Chernobyl accident). While the ^{137}Cs peak (808 Bq kg^{-1} , 26 – 27 cm) above the alunn layer (1980) clearly can be attributed to the fallout of the Chernobyl accident in May 1986, the first rise of ^{137}Cs activity concentration is much smaller (73.4 Bq kg^{-1}) and located in the lowermost sample which raises some doubt in its significance. However, the

ratio of the peak concentrations of about 11:1 confirms that the lower peak originates from the weapons fallout maximum, since it rather accurately reflects the ratio of deposition rates of both events: Integrating the Chernobyl derived ^{137}Cs present in the core gives a total deposition of $28.5 \pm 1.5 \text{ kBq m}^{-2}$ (decay corrected to May 1986), compared to the average atomic weapons fallout deposition of about 3 kBq m^{-2} in Germany (UNSCEAR 2000).

Interpreting the ^{210}Pb activity profile is not straightforward. Application of the Constant Rate of Supply (CRS) model, which allows for varying sedimentation rates, requires the total excess ^{210}Pb inventory of a core which is not available. The Constant Initial Concentration (CIC) model, which assumes time-invariant sedimentation rates, fits very well to the activity profile measured, if the 0-16 cm and the 16-49 cm sections are evaluated separately, indicating a change in the sedimentation regime at this depth. For the 0-16 cm section, however, a ^{210}Pb based chronology is in conflict with the reference points of known deposition date, and thus must be judged as unreliable. In contrast, the ^{210}Pb based sedimentation rate derived from the lower core section is in close agreement with its ^{137}Cs based value. This not only confirms our ^{137}Cs based chronology, but also its assumption of a time-invariant sedimentation rate. With the alumn layer as time reference, the ^{210}Pb chronology derived from the lower core section assigns the year $1995 \pm 2.6 \text{ y}$ to the change in the ^{210}Pb sedimentation regime. This agrees well with the time of a major change in lake treatment (stop of aeration in 1993) which may have influenced the ^{210}Pb geochemistry in the lake. Our chronology results in a total core age of $\sim 46 \text{ a}$, so the sediment contained in FIS 8/09 covers the entire eutrophication history described here, which is supported also by the obtained core data (e.g. diatoms).

4.4.2 Core lithology, XRF data and lake history phases

The most prominent feature of the core FIS 8/09 is the translucent, colloidal layer of very high water content (89 %) in 36 – 37.5 cm depth (Figure 10), compared to an average of 77 % in the rest of the core. It is the layer of the alumn-phosphorus complex deposited during the artificial P-precipitation in December 1979, which is confirmed by coincident peaks of Al- and P-counts from XRF scans (see supplements). This layer was also attributed to the P precipitation event in an earlier sediment study of Fischkaltersee conducted one year after the restoration measure (Steinberg and Fischer 1982). Therefore, it represents a chronostratigraphic marker layer dividing the core into a homogenous upper and a more heterogenous lower zone (Fig. 3). The homogenous upper part of the core (0 – 36 cm) consists of brownish-grey silts of high water content and with many macroscopic pores. These silts are interrupted by weak, irregular carbonate concretions and macroscopic plant remains. The zone directly below the alumn-layer is composed of several alternating laminae of brown-beige and light-grey silt (37.5– 40.5 cm). The homogenous lower part (40.5 – 48 cm) of FIS 8/09 consists of light-grey, fine-grained silt. High Ca-counts derived from XRF-scans indicate carbonate contents significantly higher than in the upper zone (Figure 10).

Based on the well-known history of eutrophication, restoration efforts and the chronology introduced above, both water column data and sediment proxies can be subdivided into six phases (Figure 12, Figure 13):

- A. 1963 – 1976 early eutrophication
- B. 1976 – 1980 eutrophication and meromixis
- C. 1980 – 1984 P-precipitation and permanent destratification
- D. 1985 – 1993 intermittent destratification
- E. 1993 – 2000 aided circulation
- F. 2000 – 2009 no restoration measures

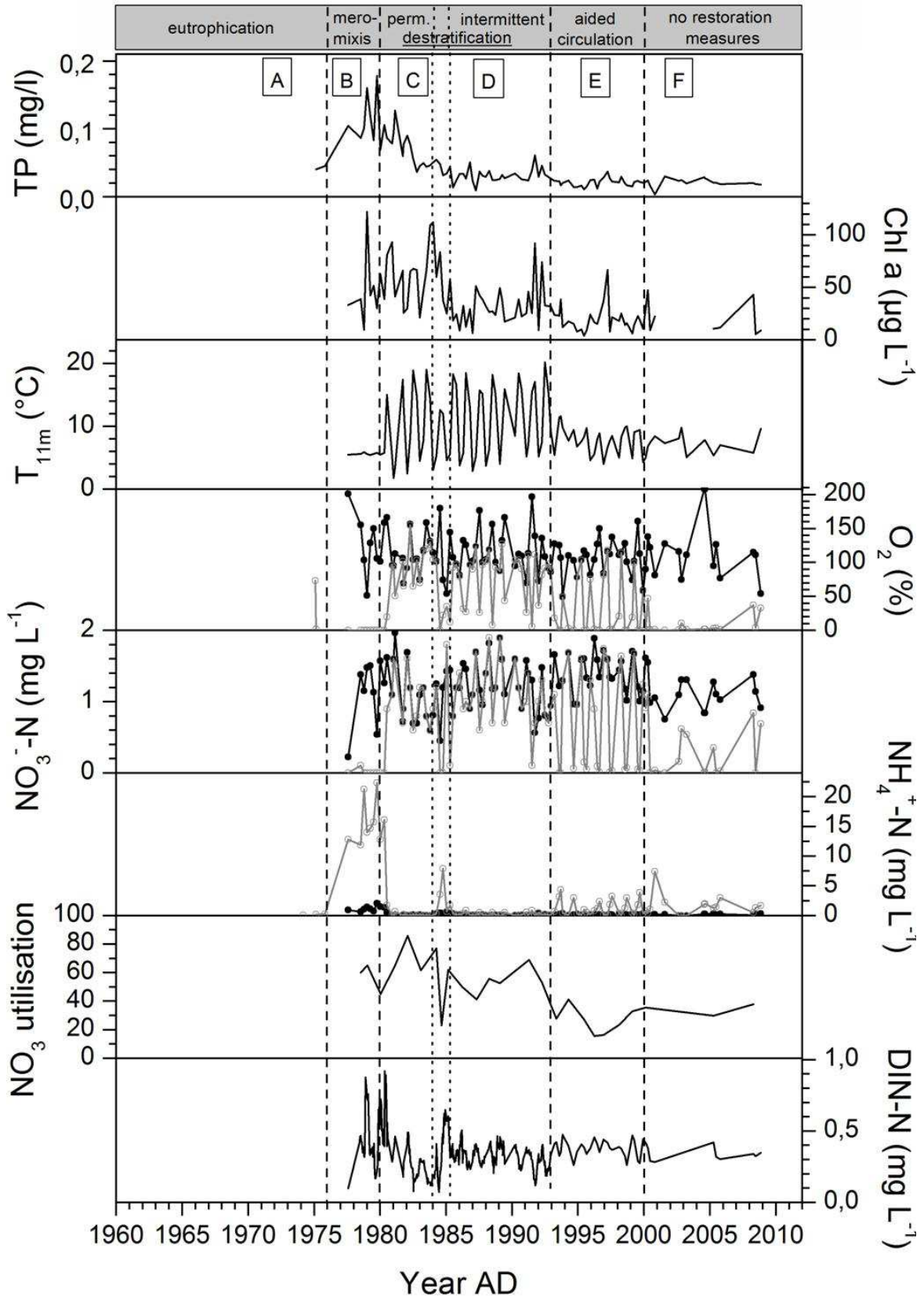


Figure 12: Record of historic water column data containing physical (T_{11m} , O_2) and chemical (concentrations of TP, Chl a, NO_3^- 0 m, 11 m, NH_4^+ 0 m, 11 m, NO_3 utilisation, DIN) parameters. For O_2 , NO_3^- and NH_4^+ closed circles represent 0 m values and open circles 11 m values. The different phases of lake history are separated through vertical dashed lines.

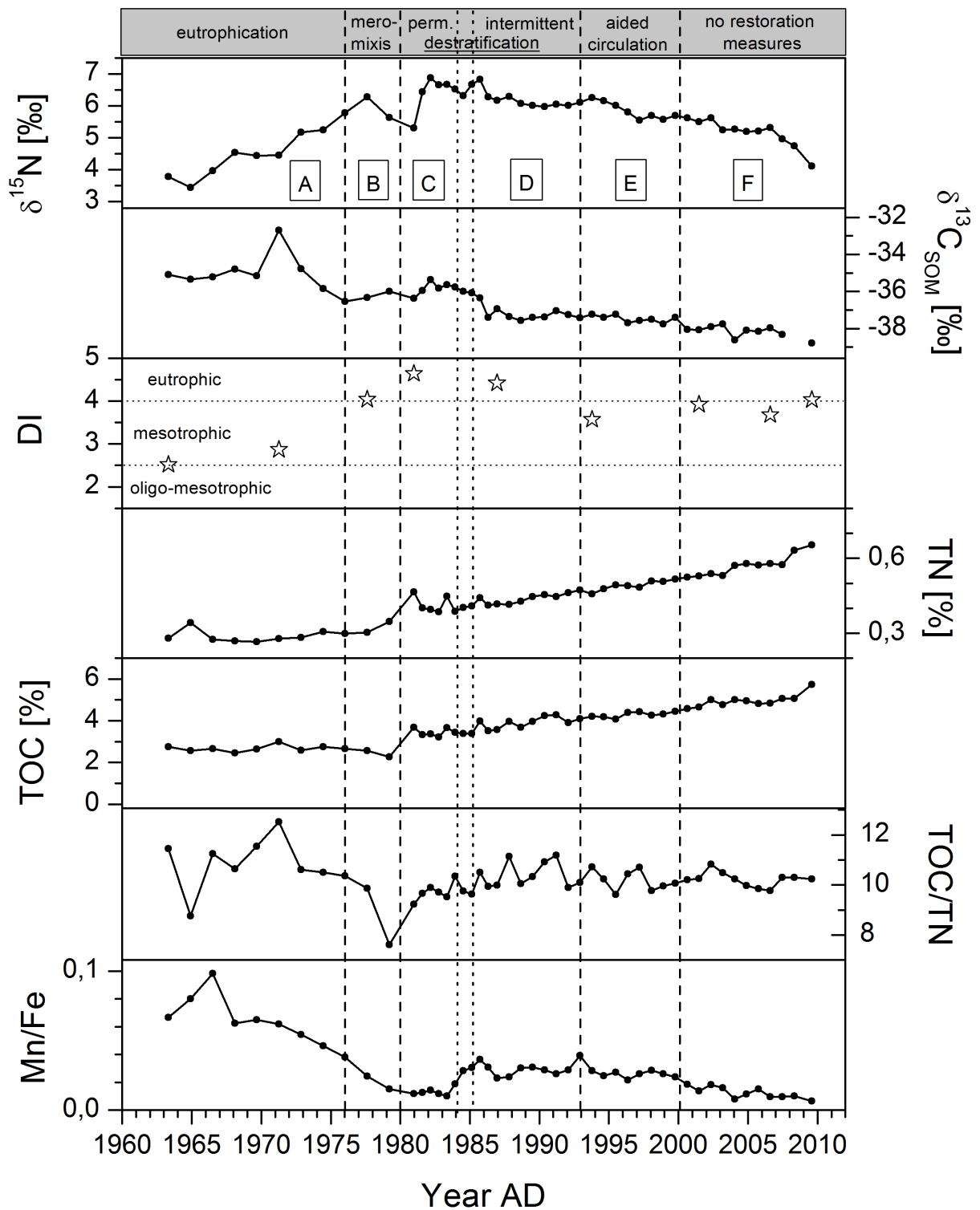


Figure 13: Isotopical ($\delta^{15}\text{N}$, $\delta^{13}\text{C}_{\text{SOM}}$), biological (DI), geochemical (TOC, TN, TOC/TN) and XRF-derived (Mn/Fe) data of core FIS 8/09. This chrono-stratigraphic profile was produced by applying the age-depth model to the core parameters of FIS 8/09.

4.4.3 Comparison between water column data and sediment proxies

Since routine measurements did not begin until 1977, water column data (Figure 12) for Phase A (1963 – 1976) is scarce. Available data show an increase in TP around 1975 (0.035 to 0.045 mg L⁻¹) and comparatively moderate NH₄⁺-N concentrations in the hypolimnion (max. 0.21 mg L⁻¹), which was still oxic in February 1975 (73 % oxygen saturation).

In the sediment proxy record (Figure 13), Phase A is characterised by a minor increase of the DI (2.5 to 2.9) indicating an change in trophic state from almost oligo-mesotrophic to mesotrophic, but with values significantly lower than in the whole record following thereafter. The δ¹³C signature remains constant until 1971, when it exhibits a sharp and isolated positive excursion (-32.7 ‰) which is followed by a decline reaching a plateau with more negative values (-36.5 ‰) until 1981. δ¹⁵N rises from a low of 3.4 ‰ to a plateau of 4.5 ‰ around 1970 and reaches a peak at 1977 (6.2 ‰). Percentages of TOC and TN remain relatively constant (averages of 0.3 % and 2.6 %, respectively) until the end of Phase B (1979) when there is a pronounced rise in both, followed by a continuous increase until maximum values (0.6 % and 5.7 %, respectively) are reached in the topmost part of the core. The TOC/TN ratio oscillates between 7.6 and 12.5 (average 10.2) without exhibiting a clear trend.

The ratio of Mn/Fe is a proxy linked to oxidation/reduction processes and therefore an indicator of anoxic conditions in lake sediments (Wersin et al. 1991, Zhu et al. 2009). In the FIS 8/09 core, the Mn/Fe values (Figure 13) exhibit a decline from 1969 towards the core top. Between 1983 and 1986, this otherwise continuously declining trend is interrupted by a minor increase.

In Phase B (1976 – 1980), in which routine measurements of water column data began, concurrent peaks in TP (max. 0.178 mg L⁻¹) and Chl a (max. 122 mg L⁻¹) (Fig. 4a) agree well with an expressed rise in DI indicating a change from mesotrophic to an eutrophic state (2.9 to 4.0) in the sediment core data (Figure 13). Constant water temperature (5.6°C) as well as O₂ and NO₃⁻-N concentrations below detection limit at the bottom of the lake indicate a meromictic state at least from 1977 on. Most noticeable are also extreme NH₄⁺ concentrations (max. 22.29 mg L⁻¹ NH₄⁺-N) that were detected in the monimolimnion from 1977 on and began to extend into surface waters thereafter. By then, NH₄⁺ was present in the trophogenic zone in significant amounts (max. 2.06 mg L⁻¹ NH₄⁺-N) and surface water nitrate utilisation (NO₃⁻

utilisation) experienced a drop of 20 %. At the same time, the positive trend of $\delta^{15}\text{N}$ exhibits a pronounced gap to a minimum (5.3 ‰) in 1981 (Figure 13).

Core signals and water column data of Phase C (1980 – 1984) are characterized by the impact of continuing eutrophication and the onset of restoration efforts. The P-precipitation measure in December 1979 managed to lower TP significantly (> 50%), but only temporary, as 14 months later TP rose again to a maximum of 0.127 mg L⁻¹. The efficacy of the permanent destratification by hypolimnion aeration, which was initiated in April 1980, is clearly visible in the extreme seasonal variations of water temperature (1.8 – 19 °C) at the lake bottom. As well, the O₂ concentration never fell below 50 % in the whole lake from 1981 until 1984. The aeration produced an initial peak in the DIN concentration, which soon was followed by a continuous decline. Concurrent with this, there is an elimination of NH₄⁺ at the lake bottom as well as in upper water layers (NH₄⁺-N > 0.14 mg L⁻¹) and a uniform concentration of NO₃⁻ in the whole water column (0.7 – 1.7 mg L⁻¹ NO₃⁻-N). In Phase C $\delta^{15}\text{N}$ also rises sharply to a maximum of 6.9 ‰ and then declines to 6.3 ‰ in 1984. At the same time, the signal of $\delta^{13}\text{C}_{\text{SOM}}$ exhibits a minor increase (1.1 ‰) followed by a decreasing trend lasting to the core top (-38.3 ‰) (Fig. 4b). At the end of this phase, Chl a reaches a distinct peak (112.3 mg L⁻¹), indicating expressed algal blooms, while TP decreases continuously (Figure 12).

From 1984 to 1985, aeration ceased for one year and NH₄⁺ accumulated again (7.9 mg L⁻¹ NH₄⁺-N). Likewise, NO₃⁻ vanished at the lake bottom, but NO₃⁻ utilisation dropped from a maximum of 85 % to 23 %. Concurrently, there is a slight elevation in $\delta^{15}\text{N}$ (+ 0.5 ‰).

Phase D (1985 – 1993) follows the aeration gap and is characterized by an overall decline in Chl a concentration (61.76 to 31.73 mg L⁻¹) and DI values (4.42 to 3.57) (Figure 12, Figure 13). After a $\delta^{15}\text{N}$ maximum (6.8 ‰) in 1985, both isotope curves show a gradual decline. Still, at the end of Phase D, there are concurrent peaks in Chl a (92.15 mg L⁻¹) and NO₃⁻ utilisation (68.75 %), and despite the ongoing intermittent destratification by artificial aeration, both oxygen and nitrate concentrations in the bottom waters are often markedly lower than in surface water layers.

In Phase E (1993 – 2000), $\delta^{13}\text{C}_{\text{SOM}}$, $\delta^{15}\text{N}$, TP, DI, Chl a and NO₃⁻ utilisation continue their negative trend. At the lake bottom, NO₃⁻ vanishes and NH₄⁺ concentrations rise concurrently on a seasonal time scale. The limited effect of the

aided circulation is visible in a considerably lower bottom water temperature (5 – 10 °C).

In Phase F (2000 – 2009) all restoration measures ceased and monitoring of water column data was only conducted in 2000, 2005 and 2008. The cessation of restoration activities resulted in a depletion of oxygen in the hypolimnion. In this period, neither $\delta^{15}\text{N}$ nor DI reached their respective levels of the beginning of the record (3.4 vs. 4.1 ‰ and 2.52 vs. 4.04), while $\delta^{13}\text{C}_{\text{SOM}}$ exhibits the lowest signature of the record at the core top (-38.9 ‰).

4.5 Discussion

4.5.1 History of eutrophication and restoration efforts

The Fischkaltersee record offers a unique possibility to compare a well-documented history of multiple anthropogenic impact, rapid eutrophication and subsequent restoration efforts with its sedimentary imprints. The lake is part of the Osterseen Lake District and most of these lakes were still in an oligotrophic state in the 1960s (Melzer 1976). Nevertheless, some lakes might already have been affected by moderate human-induced eutrophication at that time. Ongoing investigations of an lake in close proximity of Fischkaltersee indicate that the main process of eutrophication of those lakes could have started as early as 1950. Thus, the original, oligotrophic state of Fischkaltersee might already have been altered at the onset of the rapid eutrophication described here.

This is supported by the DI value at the core bottom, which indicates a trophic level significantly lower than in the entire record following thereafter. Melzer, who was the first to investigate the lake's limnology in 1974, described ongoing sewage inflow and a highly eutrophicated but still dimictic lake (Melzer 1976). Later, stratigraphic investigations of the concentrations of TP, Chl a and several elements (i.a. Mn, Al, Pb, Cd) in the sediment dated the onset of the rapid eutrophication described here to the early 1970s (Steinberg and Fischer 1982) and confirmed its rather fast progression. This agrees very well with the slight elevation in DI around 1971 and its rapid increase until 1981 present in our sediment core. Therefore, the entire sedimentation of the phase before the onset of the rapid eutrophication of Fischkaltersee as well as the phase of pollution and restoration efforts following thereafter is contained in the sediment record presented here.

Because of the discharge of salty water during annual snowmelt to the lake, Fischkaltersee switched to a meromictic status in 1975 (Steinberg and Bucksteeg 1980), but Mn/Fe indicates that the surficial sediments already became increasingly anoxic from 1970 on. This is a common result of intensified primary productivity and subsequent high OM- and P-sedimentation, which create a lasting depletion of dissolved oxygen in the sediment (Gächter and Wehrli 1998). It is important to note that this condition intensified in the sediment of Fischkaltersee and prevailed up to the end of our investigation in 2009. Moreover, it was not significantly altered by the hypolimnion aeration, whether permanent or intermittent. As the aerator used in Fischkaltersee was mounted on a steel rack approx. 1 m above ground (Steinberg and Schrimpff 1982), both the bubble plume and the resulting water current never came into direct contact with the sediment surface, where - despite an oxic bottom water zone ($> 2 \text{ mg L}^{-1} \text{ O}_2$) - anoxic conditions prevailed. This is in concordance with the findings of many aeration experiments (Fast and Tyler 1981, Bailey-Watts et al. 1987, Gächter and Wehrli 1998, Grochowska and Gawronska 2004, Teranes and Bernasconi 2000). As well, it is evident from the O_2 data of the water column that bottom waters in Fischkaltersee turned hypoxic very quickly each time the aeration ceased. In conjunction with the extreme temperature elevation in the bottom water zone during summer (max. + 13.4°C), this is of great relevance for both isotopic signals in the sediment of Fischkaltersee. As the village of Staltach was connected to a centralized sewage plant in 1981 (Steinberg and Zimmermann 1988), both the N and P load to the lake peaked around that time and so did their respective concentrations in the water column. But despite the gradual decline of sewage inflow and treatment efforts, the state of Fischkaltersee before the onset of the rapid eutrophication described here could not be re-established until present day which is obvious from the DI.

4.5.2 Sedimentary $\delta^{13}\text{C}$

Many studies attributed the controlling biogeochemical influence over $\delta^{13}\text{C}_{\text{SOM}}$ mainly to the extent of primary productivity in the phototrophic zone of a lake (Hodell and Schelske 1998, Brenner et al. 1999, Meyers and Teranes 2001, Meyers 2006, Choudhary et al. 2009, Choudhary et al. 2010). During assimilation, phytoplankton discriminates against ^{13}C (Farquhar et al. 1989). As a consequence, a ^{13}C enrichment in the remaining epilimnetic DIC pool develops, when the ^{13}C -depleted biomass is removed from the epilimnion via sedimentation. This can occur on a seasonal or multiannual time scale as DIC pools are replenished with ^{13}C -depleted carbon when biomass is remineralized again. However, periods of pronounced primary productivity and subsequent fixation of biomass in the sediment will be recorded as a $\delta^{13}\text{C}_{\text{SOM}}$ increase. Therefore, $\delta^{13}\text{C}_{\text{SOM}}$ has widely been interpreted as a proxy of primary productivity (Lücke et al. 2003).

It is evident from the data presented above that in Fischkaltersee the profile of $\delta^{13}\text{C}_{\text{SOM}}$ cannot be solely explained by primary productivity changes. $\delta^{13}\text{C}_{\text{SOM}}$ is not correlated with the development of epilimnetic primary productivity or any of its sedimentary proxies (DI, Chl a, TP) in the later stages of eutrophication of Fischkaltersee.

With the exception of the defined positive excursion in 1971 during the onset of eutrophication, the overall reaction of $\delta^{13}\text{C}_{\text{SOM}}$ to eutrophication as well as to all restoration efforts is a continuous negative trend. This is shown by the most depleted $\delta^{13}\text{C}_{\text{SOM}}$ signatures (minimum -38.8 ‰) in the youngest samples of the record, when Fischkaltersee was already in a state of trophic recovery. Even before the onset of the rapid eutrophication in 1970, the isotopic signature of organic carbon in the sediment $\delta^{13}\text{C}_{\text{SOM}}$ was constant but quite ^{13}C -depleted (average -35.1 ‰).

These rather low values are more negative than common $\delta^{13}\text{C}_{\text{SOM}}$ signatures of lacustrine algal matter and also lake sediment (Meyers and Teranes 2001), but are in good agreement to the isotopic signature $\delta^{13}\text{C}_{\text{SOM}}$ (-30 to -37 ‰) encountered by the investigation of Teranes and Bernasconi 2005 in the sediment of hypereutrophic Baldeggersee, Switzerland. The authors of this study found the $\delta^{13}\text{C}_{\text{SOM}}$ profile to be caused by variations in the relative input of both ^{13}C -enriched photoautotrophic and microbial biomass, which is known to have a much more depleted signature.

Likewise, the $\delta^{13}\text{C}_{\text{SOM}}$ record of Fischkaltersee cannot be derived from the input of photoautotrophic biomass alone, whose carbon isotopic signature typically is about -28 ‰ (Meyers and Lallier-Verges 1999).

Particularly in eutrophicated lacustrine environments such low $\delta^{13}\text{C}$ signatures have been associated with significant influence of ^{13}C -depleted OM derived from heterotrophic sources (Lehmann et al. 2004, Teranes and Bernasconi 2005, Daskalou et al. 2009), as the excess availability of nutrients not only increases primary productivity, but also OM sedimentation and subsequent microbial reworking processes (Liikanen and Martikainen 2003). Together with the resulting anoxic conditions in the water column and/or sediment, eutrophication produces ideal conditions for an expansion of the heterotrophic community and the associated carbon cycling processes, i.e. sulfate reduction, denitrification, chemoautotrophy, methanogenesis and methanotrophy (Hollander and Smith 2001, Liikanen and Martikainen 2003). Among those, the formation of methane in the anoxic part of the sediment and its subsequent oxidation in the upper water column and reintegration into the DIC pool play a key role for the isotopic signal $\delta^{13}\text{C}_{\text{SOM}}$ in the sediment: Microbial methane typically is quite depleted in $\delta^{13}\text{C}$ (-110 ‰ to -50 ‰) (Whiticar et al. 1986, Whiticar 1999) and significant amounts (up to 50 %) of the sedimenting carbon are recycled into methane (Fallon et al. 1980, Kelly and Chynoweth 1981). Methanotrophic processes that oxidize CH_4 and thus reintegrate it into the epilimnetic DIC pool add another step of additional isotopic depletion, as the associated fractionation effect is -16 ‰ to -30 ‰ (Summons et al. 1994). This process can be of quantitative significance: Ogrinc et al. 2002 found that in Lake Bled, a carbonate-rich, subalpine lake in Slovenia, up to 78 % of DIC in pore water originates from methanogenesis.

Recently, it has been shown using data from 50 lakes in western Ireland that, depending on the extent of bottom water anoxia, methane production in anaerobic lake sediments can be of greater influence on sedimentary $\delta^{13}\text{C}_{\text{SOM}}$ than primary production (Woodward et al. 2012).

Smith and Hollander (2001) introduced a conceptual model on the response of $\delta^{13}\text{C}_{\text{SOM}}$ to cultural eutrophication: For a wide TP range (approximately 0.05 to 0.175 mg L^{-1}), they attribute the dominating influence on the carbon isotopic signal to the extent of microbial carbon cycling processes in the lake (i.e. methanogenesis and methanotrophy), which are superimposed on the signal of the photoautotrophic

biomass. Therefore, a negative isotopic trend in sedimentary carbon is predicted following eutrophication in the TP range named above. The isotopic signal of primary productivity processes will control $\delta^{13}\text{C}_{\text{SOM}}$ only when TP is below or above the proposed TP thresholds, which were interpolated from water column data and $\delta^{13}\text{C}_{\text{SOM}}$ profiles of two lakes of different degrees of eutrophication.

This model is consistent with the $\delta^{13}\text{C}_{\text{SOM}}$ profile observed in Fischkaltersee: As the eutrophication process proceeded exceptionally fast here, it is reasonable to assume that the lower TP threshold, above which microbial input will dominate, was crossed rather quickly already in the 1970s. Thus, the impact of the intensifying primary productivity on the $\delta^{13}\text{C}_{\text{SOM}}$ signal in the sediment was constrained to the defined positive excursion of $\delta^{13}\text{C}_{\text{SOM}}$ in 1971. From 1971 on, the almost continuous decline in the signal indicates an increasing imprint of ^{13}C -depleted microbial processes on the sediment, either uncoupled to epilimnetic primary productivity via sedimentation of depleted heterotrophic biomass or coupled through methanogenesis, subsequent oxidation and reintegration in the surface water DIC pool.

Although no data is available on the isotopic composition of DIC or the extent of methane production in Fischkaltersee, insight into the interactions of primary productivity, methanogenesis and methanotrophy can be gained from an investigation on the pelagic bacteria population (0 – 11 m), which was conducted before the onset of artificial aeration by Steinberg and Niesslbeck (1981). They found that bacteria population maxima preceded those of phytoplankton, the latter using DIC as substrate that originated from methane produced in the monimolimnion and sediment that was subsequently oxidized in upper water layers. This process is likely to have intensified through the artificial aeration, as the sediment remained anoxic, but oxygenated bottom waters allowed for a quantitative oxidation of the produced CH_4 all year round. Also, both OM sedimentation and bottom water temperature increased considerably, which has the potential to promote methanogenesis further, as methane production is known to be a direct function of both OM input and temperature (Kelly and Chynoweth 1981). It is documented that the aeration in Fischkaltersee was accompanied by a fivefold increase in abundance of heterotrophs (Steinberg and Schrimpf 1982).

The negative trend of $\delta^{13}\text{C}_{\text{SOM}}$ continues towards the youngest part of the sediment core. Consequently, during the course of the eutrophication of Fischkaltersee a TP threshold was crossed around 1971 and thereafter microbial

processes dominated over the effect of primary productivity on carbon isotopes to the present day. $\delta^{13}\text{C}_{\text{SOM}}$ values further imply that TP never crossed an upper threshold, above which algal biomass again controls $\delta^{13}\text{C}_{\text{SOM}}$ (according to the conceptual model of Hollander & Smith 2001). It is also interesting to note that the $\delta^{13}\text{C}_{\text{SOM}}$ signature of the sediment of Fischkaltersee was already more ^{13}C -depleted (average -35.1 ‰) in the period before the onset of the rapid eutrophication process (1963 – 1970) than it is in similar lakes (Drew et al. 2008, Choudhary et al. 2009, Lu et al. 2010). According to that, microbial carbon cycling has always provided a significant input to DIC and the sediment in Fischkaltersee.

4.5.3 Sedimentary $\delta^{15}\text{N}$

The $\delta^{15}\text{N}$ value of bulk sedimentary nitrogen has been used as a proxy of paleoproductivity in several investigations of lake eutrophication (e.g. Talbot 2001). Analogous to carbon uptake, phytoplankton discriminates against the heavier isotope ^{15}N during DIN uptake (Sigman et al. 1999), where the degree of isotopic fractionation depends on the assimilated N form (NO_3^- vs NH_4^+). Given a sufficient consumption of N in surface waters, the resulting depletion of ^{14}N will be reflected in a ^{15}N increase in the remaining DIN pool and of the subsequently produced photoautotrophic biomass. Marine studies revealed a strong positive correlation between $\delta^{15}\text{N}$ of phytoplankton and the extent of surface-water nitrate depletion, i.e. primary productivity (Altabet and Francois 1994). But for freshwater systems, this correlation was considered to be rather weak, because lacustrine primary productivity is limited more by P than by N, so that the consumption of the DIN pool shows less impact on $\delta^{15}\text{N}$ of phytoplankton (Lehmann et al. 2004). However, Teranes and Bernasconi (2000) were able to confirm a positive correlation between $\delta^{15}\text{N}$ and primary productivity rates for the lacustrine environment of hypereutrophic Baldeggersee as well. They show that $\delta^{15}\text{N}$ of newly produced photoautotrophic biomass is positively correlated to the amount of nitrate depletion in surface waters and its signal is closely recorded in the weighted average N isotopic composition of sedimenting organic matter and consequently in $\delta^{15}\text{N}$ of sediment recently deposited.

The results of our investigation provide additional evidence that sedimentary $\delta^{15}\text{N}$ can be a useful record of the nitrate utilisation in the epilimnion of lakes. In Fischkaltersee, the profile of $\delta^{15}\text{N}$ corresponds well to the overall development of the

eutrophication process, i.e. the intensity of primary productivity as is represented more accurately by Chl a and DI than by TP (Wetzel 2001).

When compared directly to NO_3^- utilisation, the relationship becomes obvious: $\delta^{15}\text{N}$ values are most enriched (+ 6.9 ‰) when NO_3^- utilisation was most pronounced (85 %) in 1982.

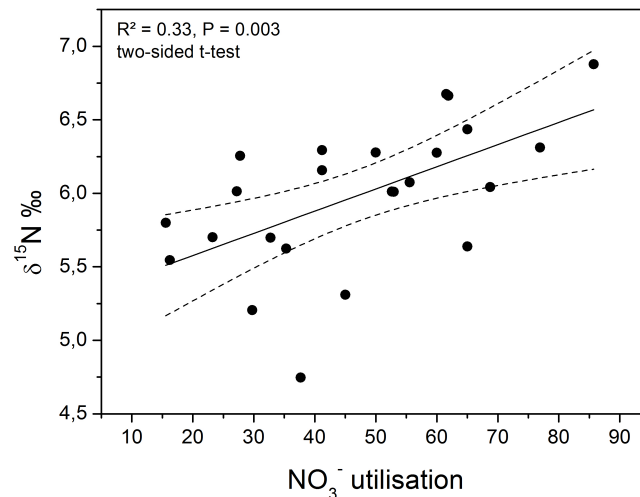


figure 14: $\delta^{15}\text{N}$ isotopic signature of FIS 8/09 vs NO_3^- utilisation in the epilimnion. Dotted lines indicate the confidence band for the given parameters of the linear correlation.

Nevertheless, the rather weak ($R^2 = 0.33$) linear correlation of NO_3^- utilisation and $\delta^{15}\text{N}$ (Figure 14) reveals that the effect of primary productivity on $\delta^{15}\text{N}$ can be confounded by other influences:

Some precision of the correlation might be lost as well to the fact, that NO_3^- utilisation was calculated for each individual year as the seasonal depletion of the surface water NO_3^- pool, according to Lehmann et al. (2004). The $\delta^{15}\text{N}$ values on the other hand were obtained from sampling the sediment core in slices of 1 cm, which might not always represent the exact integrated mean of the respective time period.

As mentioned above, the fractionation effect during DIN assimilation depends on the N form incorporated. For ammonium the associated fractionation ($\epsilon = -10$ ‰, Fogel and Cifuentes 1993) has been shown to be larger than for nitrate assimilation, so that uptake of NH_4^+ will result in more depleted $\delta^{15}\text{N}$ of organic matter. Due to an extremely elevated ammonium concentration in bottom waters during the meromictic phase (Phase B) and the aeration gap in the years 1984 – 1985, NH_4^+ was present in significant amounts in the phototrophic zone of Fischkaltersee at that time. Its direct uptake by primary producers is visible in concurrent drops of $\delta^{15}\text{N}$ as well as of NO_3^- utilisation during those periods.

We conclude from this, that in Fischkaltersee both the intensity of surface water DIN utilisation and the form and isotopic composition of DIN assimilated by phytoplankton are the main controls on $\delta^{15}\text{N}$ of sedimentary organic matter.

It is important to note that several other processes in the rather complex lacustrine N cycle have the potential to impart strong trends to the nitrogen isotopic signal in the sediment, which makes detailed knowledge about the underlying processes in the lake essential for the interpretation of the sedimentary $\delta^{15}\text{N}$ record.

The TOC/TN of SOM in Fischkaltersee is rather constant (10.2), but somewhat higher than expected for pure algal matter, which typically ranges between 7-9 (Meyers and Teranes 2001). This might be a sign of active denitrification occurring during early sedimentation, because N-rich products are preferentially degraded (Meyers and Teranes 2001, Lehmann et al. 2002). Although a substantial amount of both C and N can be lost to early diagenesis after sedimentation (approx. 20 % and 35 %, respectively), it is encouraging for the interpretation of sedimentary $\delta^{13}\text{C}_{\text{SOM}}$ and $\delta^{15}\text{N}$ that the associated isotope effects are only minor (max. +1.5 ‰ and - 0.7 ‰, respectively; Gälman et al. 2009) and, thus the original signals are preserved.

Nevertheless, denitrification in the water column is a source of considerable N loss to the DIN pool of a lake, which must also be considered in our interpretation, as it is associated with a potentially enormous enrichment of ^{15}N in the remaining nitrate pool (+14 to +26 ‰, Teranes and Bernasconi 2000) and the extent of this strictly anoxic process strongly depends on phases of stagnation. Hodell and Schelske 1998 interpret a continuous 6 ‰ increase in $\delta^{15}\text{N}$ in the sediment of Lake Ontario as a sign of increased water column denitrification promoted by several meromictic episodes, which are the result of intensified primary productivity. Therefore, it is possible that the $\delta^{15}\text{N}$ increase in Phase A was caused by increasing denitrification. However, if water column denitrification would have been the main cause for the $\delta^{15}\text{N}$ profile observed in Fischkaltersee, one would expect a strong drop of the signal once the hypolimnion aeration was initiated, as it eliminated anoxic zones in the water column. Thus we conclude that water column denitrification never has been the most significant influence to sedimentary $\delta^{15}\text{N}$ in Fischkaltersee.

Nevertheless, there is evidence for extensive denitrification in Fischkaltersee: In the first months following the onset of artificial destratification, there is a twofold increase in DIN (0.41 to 0.89 mg N L⁻¹). This is probably due to the oxidation of dissolved-organic nitrogen (DON) to nitrate, which appears in the hypolimnion from

then on. During Phase C, when permanent aeration would not allow for water column denitrification, DIN decreases considerably (0.89 to 0.07 mg N L⁻¹). This continuous decrease could be a result of denitrification in the anoxic sediment. As mentioned above, both the extreme increase in temperature and the oxygenation of bottom water layers are likely to have promoted microbial processes in the sediment, i.e. denitrification, as it depends on NO₃⁻ as a substrate and the activity of nitrification is known to be regulated by O₂ concentration (Grochowska and Gawronska 2004; Jensen et al. 1993).

Due to rate limitations caused by the transport therein, sediment denitrification is considered to exhibit only a minor isotopic fractionation (Brandes and Devol 1997). Thus, although quantitatively of considerable importance, it would not influence the isotopic signature of DIN to the extent of water column denitrification (Teranes and Bernasconi 2000).

Increasing input of heterotrophic biomass could as well be responsible to a certain amount for the profile of sedimentary δ¹⁵N in Fischkaltersee during 1963 to 1986, as it will also elevate δ¹⁵N because there is an increase of 3 to 4 ‰ for each trophic level, (Deniro and Epstein 1981, Peterson and Fry 1987). Therefore, especially the fivefold increase in abundance of heterotrophs which occurred as a result of the permanent destratification from 1980 on, could have contributed to the expressed increase in δ¹⁵N thereafter.

It is well known that human sewage as well as manure, both used as agricultural fertilizers, can be extremely enriched in ¹⁵N (+ 5 to + 20‰, Talbot 2001), because land-based denitrification allows for an considerable ¹⁴N loss.

Although neither the amount of the external N load nor its isotopic composition have been investigated during the anthropogenically induced eutrophication of Fischkaltersee, there is a good agreement between the overall profile of sedimentary δ¹⁵N and the history of sewage input in Fischkaltersee: Most enriched δ¹⁵N signals in the sediment record appear between 1982 and 1986, while due to the launch of the local sewage plant, the external N load to the lake peaked around 1981. A slow decline of this input is likely as well because considerable subsequent desorption from the saturated aquifer is documented for the concurrent P input (Steinberg and Zimmermann 1988). Therefore, despite a significant effect of epilimnetic nitrate utilisation by primary productivity, a factor influencing δ¹⁵N in Fischkaltersee could as well be the isotopic signature of the external N load.

4.6 Conclusions

In the past, primary productivity was thought to be the main biogeochemical influence controlling $\delta^{13}\text{C}_{\text{SOM}}$, thus rendering the latter an ideal proxy indicator of paleoeutrophication.

Particularly in anthropogenically eutrophicated systems this assumption might not always be valid. Here, the common anoxic conditions allow for an intensification of microbially mediated carbon cycling processes that have the potential to confound the effect of primary productivity on $\delta^{13}\text{C}_{\text{SOM}}$.

Based on their observations in two differently eutrophicated lakes, Smith and Hollander (2001) introduced a conceptual model which, for a certain TP range (approx. 0.05 to 0.175 mg L⁻¹), attributes the dominating impact on $\delta^{13}\text{C}_{\text{SOM}}$ to the extent of methanogenesis and methanotrophy in a lake. Since then, this effect has been confirmed to be of practical relevance (Woodward et al. 2012).

Our data provide additional conclusive evidence for the relevance of this model for $\delta^{13}\text{C}_{\text{SOM}}$ in anthropogenically eutrophicated lakes. In Fischkaltersee, its well-documented history of rapid eutrophication, multiple human impact and subsequent restoration efforts allows for a validation of the concept proposed by Smith and Hollander, particularly for the concept of P-thresholds controlling the dominant input to $\delta^{13}\text{C}_{\text{SOM}}$. Here, the impact of primary productivity on the carbon isotopic signature of SOM is constrained to the early phase of eutrophication (TP > 0.04 mg L⁻¹). At higher TP concentrations, the intensity of microbial processes, i.e. methanogenesis and methanotrophy, becomes the dominating influence to $\delta^{13}\text{C}_{\text{SOM}}$.

It is important to emphasize that in Fischkaltersee $\delta^{13}\text{C}_{\text{SOM}}$ is not linearly related to the TP concentration in the water column, as this is an important implication constraining the applicability $\delta^{13}\text{C}_{\text{SOM}}$ for investigations on lacustrine paleoeutrophication.

Other investigations considered the extent of stagnation and anoxia in the water column to control the extent of methanogenesis and therefore its impact on $\delta^{13}\text{C}_{\text{SOM}}$. (Teranes and Bernasconi 2001).

In Fischkaltersee, both the permanent as well as the intermittent destratification had no significant effect on the negative trend of $\delta^{13}\text{C}_{\text{SOM}}$. Our investigation reveals that water column anoxia is not necessarily a prerequisite for the domination of microbially mediated carbon cycling processes. Their influence on $\delta^{13}\text{C}_{\text{SOM}}$ can

prevail as long as one compartment, i.e. the surficial sediments, remains anoxic, which is a common result of increased OM sedimentation rates during eutrophication.

On the other hand, our results suggest that $\delta^{15}\text{N}$ is a useful indicator of lacustrine primary productivity even if its linear correlation to NO_3^- utilisation can be weakened by various other processes in the rather complex N cycle. However, because of this, a detailed knowledge about the underlying processes in the water column is essential for the interpretation of $\delta^{15}\text{N}$ in terms of paleoproductivity.

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5 Impact of anthropogenic eutrophication on sedimentary carbon and nitrogen isotope records from a meromictic and a holomictic basin of Lake Eishaussee (S-Germany)

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Running title: Impact of anthropogenic eutrophication on isotope records from Lake Eishaussee

5.1 Abstract

In this investigation we report on the impact of a biphasic anthropogenic eutrophication process on the sedimentary records of Eishaussee, a small hard-water lake (S-Germany). Eishaussee consists of both an meromictic (EHW) and an holomictic basin (EHE) and was affected by anthropogenic nutrient loading in two phases peaking around AD 1828 and AD 1986 respectively, as is reflected by the sedimentary diatom index (DI) and the water column total phosphorus concentration (TP) from EHW. We compare the impact of the eutrophication process on carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopes of sedimentary organic matter (SOM) to parallel trends of several geochemical signals (%TN, %TOC, TOC/TN) in the sediment core records spanning ca. 260 (EHE) and 300 (EHW) years. Both core records contain the sedimentation sequence prior to the onset of meromixis in EHW in AD 1828, which resulted from elevated OM sedimentation induced by the first anthropogenical eutrophication. Before as well as after the the onset of meromixis there is an offset in $\delta^{13}\text{C}_{\text{SOM}}$ between EHE and EHW (mean: +0.82‰ and +0.77‰ respectively), while the overall reaction to both eutrophication episodes is a pronounced negative drop in signal (EHW: -2.62‰ and -3.53‰; EHE:-0.96‰ and -2.25‰) concordant in both cores, resulting in values as low as -37.65‰ (EHW) and -35.73‰ (EHE). As the offset in $\delta^{13}\text{C}_{\text{SOM}}$ between both cores is present before the onset of meromixis in EHW, we conclude that it is not an effect of differences in water column processes, but in postburial diagenetic effects. The concordant drop of $\delta^{13}\text{C}_{\text{SOM}}$ in both cores in reaction to each trophic level increase is produced by methanogenetic processes dominating over a photoautotrophic signal. On the other hand, while $\delta^{15}\text{N}_{\text{SOM}}$ exhibits a mean offset of +0.77‰ between EHE and EHW and a pronounced drift in the pre-meromictic phase which cannot be directly related to the DI development, the following increases during the two phases of eutrophication are likely to be a combined result of increased primary production and denitrification.

5.2 Introduction

The organic carbon ($\delta^{13}\text{C}$) and total nitrogen ($\delta^{15}\text{N}$) isotopic composition of sedimentary organic matter (SOM) has routinely been used in marine and lacustrine investigations as a proxy indicator for the intensity of various biological processes in the water column (Hodell and Schelske 1998, Choudhary *et al.* 2010, Lücke *et al.* 2003, Meyers 2006, Woodward *et al.* 2012). Many lacustrine studies used the stratigraphic variations of $\delta^{13}\text{C}_{\text{SOM}}$ and, to a lesser extent, that of $\delta^{15}\text{N}_{\text{SOM}}$, to reconstruct historic increases in trophic level caused by intensification of photoautotrophic primary productivity as a consequence of anthropogenic eutrophication (Teranes and Bernasconi 2005, Daskalou *et al.* 2009, Braig *et al.* 2013).

For $\delta^{13}\text{C}_{\text{SOM}}$, the rationale supporting this approach is that during C assimilation, algae favour the lighter isotope ^{12}C over ^{13}C (Farquhar *et al.* 1989), which produces a corresponding ^{13}C -enrichment in the remaining dissolved inorganic carbon (DIC) pool. As during periods of elevated primary productivity the epilimnetic DIC pool is progressively consumed, the resulting enrichment in ^{13}C will be reflected as well in the biomass produced and deposited in the sediment thereafter. Therefore, in lakes where primary productivity is the main control of the carbon isotopic composition of SOM, periods of elevated primary productivity will be recorded as an increase in $\delta^{13}\text{C}_{\text{SOM}}$ (Hollander and McKenzie 1991; Brenner *et al.* 1999).

For some lakes, a similar relationship has been shown to exist between the intensity of epilimnetic primary production and $\delta^{15}\text{N}_{\text{SOM}}$ (Hodell and Schelske 1998, Teranes and Bernasconi 2000, Braig *et al.* 2013), although a sufficient consumption of the surface water dissolved inorganic nitrogen (DIN) pool is rather seldom in lacustrine systems, where primary productivity is limited more often by the availability of phosphorus than of nitrogen (Wetzel 2001, Lehmann *et al.* 2004).

But as only a small fraction (1-35% of C, Lehmann *et al.* 2002; Lehmann 2004) of OM produced during assimilation in the upper photic zone reaches the sediment surface directly, secondary recycling processes can also leave strong imprints on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM, thus obscuring the signal of primary productivity. A major part (>85% Eadie *et al.* 1984, Meyers and Ishiwatari 1993) of the sinking OM is oxidated directly in the upper water layers and in the oxic part of the hypolimnion and thus

recycled, but several investigations revealed that in particular processes associated with anaerobic degradation, like the formation and oxidation of methane and denitrification, have the potential to become the dominant control on the isotopic C and N signatures of SOM (Hodell and Schelske 1998, Hollander and Smith 2001, Woodward *et al.* 2012).

While it is a well understood fact that during sedimentary degradation mass loss of SOM as well as modification of its bulk composition are more expressed under oxic conditions and SOM preservation on the other hand is generally higher in anoxic environments (Meyers and Teranes 2001), conflicting evidence exists on the effect of postdepositional diagenesis on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM and how it is controlled by the availability of molecular oxygen at lake bottom.

Considerable loss of bulk mass of OM occurs within the sediment after deposition (e.g. 20 – 23% of C, 35% of N in 27 a, Gälman *et al.* 2008). However, the reported degree of isotopic alteration due to postburial diagenetic processes differs significantly. Hodell and Schelske (1998) report that in lake Ontario mass reduction through sedimentary diagenesis continued under oxic conditions until the OM reached deeper anoxic horizons, but the initial carbon isotopic signature of SOM remained unaltered throughout the entire sedimentation process. Gälman *et al.* (2009) on the other hand found that in a dimictic lake with a periodical anoxic hypolimnion both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM changed significantly ($\delta^{13}\text{C}$: +0.4 to +1.5 ‰; $\delta^{15}\text{N}$: -0.3 to -0.7 ‰) after burial concordant with the considerable mass loss cited above, whereas the results of Teranes and Bernasconi (2000) indicate that in the artificially aerated lake Baldeggersee $\delta^{15}\text{N}_{\text{SOM}}$ preserves the original signal of water column processes as recorded by sediment traps.

Because the extent and quality of postburial alteration is of considerable importance for the reconstruction of water column processes by $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM, it needs to be clarified to which extent the original isotopic input signal is preserved or modified in the sediment under different oxygenation conditions.

In this study, we report on the impact of several phases of cultural eutrophication on Eishaussee, a small hardwater lake in South Germany consisting of both a holomictic as well as a permanently meromictic basin, and reveal how this impact is preserved in the signals of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM in an oxic and an anoxic environment, respectively.

5.3 Methods

5.3.1 Site description

Eishaussee (47°47'3.16" N, 11°19'0.69" W, 588 m a.s.l.) is part of the pre-Alpine lake district Osterseen located in Bavaria, Southern Germany and drains an east-west oriented side chain (Staltach side chain) to the main chain of lakes spanning in south-north direction (Figure 15).

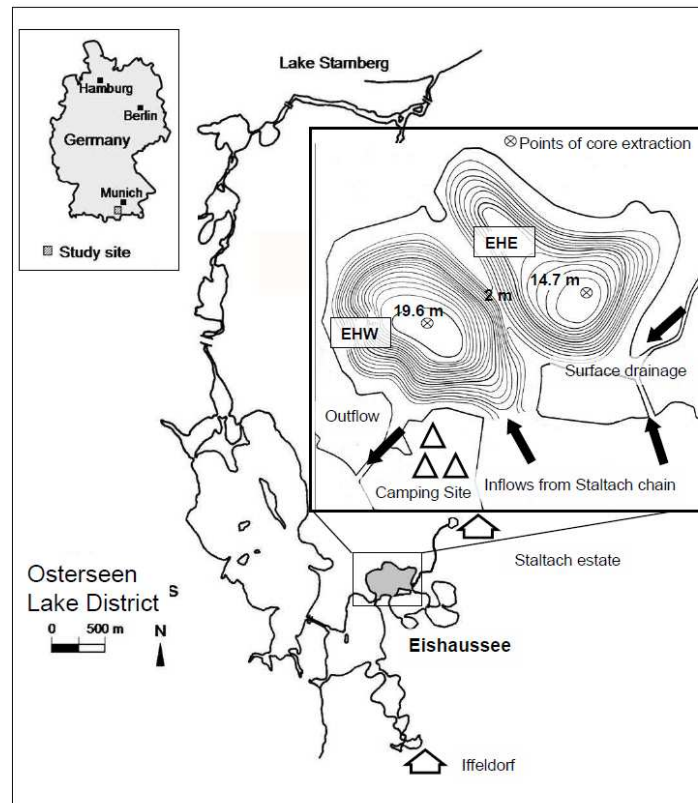


Figure 15: Outline map of the geographic location of the Osterseen Lake District and the position of the investigated lake, Eishaussee (grey filling). The position of the Staltach estate and the camping site are given. The bathymetric map reveals the form and maximum depth of both basins and shows the point of core extraction and the inflows to Eishaussee.

The hardwater lake has a mean depth of 6.6 m, total volume of $511.3 \times 10^3 \text{ m}^3$, surface area of $77.2 \times 10^3 \text{ m}^2$ and is divided into two sub-basins of different maximum depths and volumes (west basin EHW: 19.6 m; $297 \times 10^3 \text{ m}^3$ / east basin EHE: 14.7 m; $214.7 \times 10^3 \text{ m}^3$) by an underwater ridge approx. 2 m under the water surface (Zorell 1941). The shape of both basins with relatively high depths evidences their formation as kettle lakes at the end of the Last Glacial (Rothpletz 1917, Bludau and Feldmann 1994).

The first mentioning of Eishaussee was in the land survey by Philipp Apian from the 16th century (Bukovec and Exner 1994). Apian mentions the lake as two separate

basins (“vorder and hinder Runzell”) possibly indicating that the ridge separating the two lake basins was above the water surface during that time (Bukovec and Exner 1994). However, Zorell, who was the first to investigate the limnology of the Osterseen lake district in 1929 and in 1941, found that ridge already submersed and ascribed this to an historic landslide (Zorell 1941). He also found stable meromictic conditions in the westward basin of Eishaussee (EHW) and described a non-circulating bottom water layer containing hydrogen sulphide (H₂S) and exhibiting a temperature increase of 0.88°C from 14 m towards 19 m depth (Zorell 1941). While the shallower eastward basin (EHE) is holomictic (Braig, unpublished results), the permanent meromictic character of EHW was confirmed by all investigations thereafter (Melzer 1976, Raeder 1990, Braig *et al.* 2010).

The main water supply to the Osterseen lake district is punctual subsurface inflow of groundwater (Melzer 1976), but Eishaussee currently receives its inflow mostly from surface runoff and the upstream lakes of the Staltach side chain. However, there is a sporadically active surface drainage to EHE originating from a now dried-out small lake close to the rural estate of Staltach (Fig. 1). In the 19th century this estate housed an early industrial complex (railway forge, peat cutting, pig fattening and brewery) (Bukovec and Exner 1994).

An investigation of the oxygen isotope variations in the water column over one year revealed an isotopic composition of the monimolimnion different to the upper water layers of Eishaussee (Braig *et al.* 2010). Moreover, considerable ¹⁸O enrichment was detected in the mictic upper zone relative to the adjacent lake Fohnsee and to the ground water indicating high water residence time in Eishaussee.

Eutrophication history and limnology

The well documented part of cultural eutrophication of the Osterseen lake district began in the middle of the 20th century by direct sewage discharge and runoff from agricultural areas into the lakes close to the growing villages of Staltach and Iffeldorf, and spread in the lakes downstream from there (e.g. Melzer 1976, Raeder 1990, Bukovec and Exner 1994).

The process accelerated from 1970 on, as Eishaussee was affected by the rather fast and severe eutrophication of Fischkaltersee (Braig *et al.* 2013), which is the head lake of the Staltach side chain. Additionally, a caravan camping site was built in close proximity south of EHW in 1967 (Fig. 1). Since that period the lake district was used with increasing intensity as a recreation area with up to 10,000 visitors on weekends

(Bukovec and Exner 1994). Both the camping site and Staltach were not connected to a centralised sewage treatment plant until 1982, and accordingly, water column concentrations of Total Phosphorus (TP) in Eishaussee peaked around that time (Raeder 1990).

The phytoplankton succession in Eishaussee has been investigated in 1986 and 1987 (Raeder 1990). Two diatom blooms were registered: the first occurred in May and a second, weaker peaked in June. Both were characterized by high abundances of the centric diatom *Cyclotella comensis* (up to 1345 individuals per ml). Later peaks of phytoplankton biomass in July and September were dominated by the thiophile Cryptophyceae *Cryptomonas phaseolus*, which commonly exists at the oxygen-sulphide interface in meromictic lakes (Garcia-Gil *et al.* 1993, Gasol *et al.* 1993, Gervais 1998, Camacho *et al.* 2001). Biogenic calcite precipitation is frequently observed in the Osterseen chain of lakes, as the water is rich in calcium carbonate (Eishaussee: 70 mg Ca²⁺ L⁻¹, Melzer 1976). It is induced by the withdrawal of dissolved CO₂ caused by phytoplankton assimilation and therefore accompanies the seasonal phytoplankton peaks named above (Raeder 1990, Wetzel 2001). Both the mixolimnion in EHW and the whole water column of EHE are dimictic and exhibit uniform signatures of temperature, oxygen saturation, pH and conductivity during annual overturn (Braig, unpublished results). The monimolimnion below the chemocline in EHW at 14 m depth is characterized by long-term stable conditions of anoxia, low pH, high conductivity and the presence of H₂S (Zorell 1941, Melzer 1976, Braig *et al.* 2010). From 1974 to 2005, the annual mean of Secchi depth in EHW varied between 4 and 6 m, while intraannual variations exhibited the same range (Melzer 1976, Raeder 1990, unpublished results).

5.3.2 Field and laboratory methods

Sediment cores were collected in July 2008 (EHW 07/08; 45.5 cm) and in August 2009 (EHE 08/09; 48.5 cm) from the deepest part of each respective basin (Figure 15) using an UWITEC gravity corer. Cores were stored in PVC tubes in the dark at +4°C until they were split lengthwise in two halves. One half of each core was photographed and described lithologically and then analysed for relative element content by X-ray fluorescence (XRF) scanning (Mo tube, 200-µm (EHW) and 1000-µm (EHE) step size) with an ITRAX XRF core scanner (Cox Analytics, Sweden) (Lüder *et al.* 2006, Croudace *et al.* 2006). After the non-destructive analyses, the core half was sampled continuously and volumetrically in intervals of 1 cm. The resulting subsamples were weighed and freeze-dried for the determination of dry density and water content.

Samples of the other core half were used for ^{137}Cs and ^{210}Pb dating by determination of their activity concentrations (Nehyba *et al.* 2011). A γ -ray spectrometer with a high-purity Germanium well detector (Canberra, 36.6 % relative efficiency) was used. The activity of unsupported (excess) ^{210}Pb was obtained by subtracting ^{226}Ra activity, which is in equilibrium with the ^{210}Pb already present in the sediment minerals, from total ^{210}Pb activity.

Sediment ages were calculated from ^{210}Pb activity patterns applying a constant initial concentration (CIC) model. Since this approach adequately reproduced the depth profiles measured, no attempt was made to apply more sophisticated models. In both cores, the peaks of maximum ^{137}Cs -activity caused by the 1986 Chernobyl fallout deposit were used as second, independent time marker.

For elemental and isotopic analysis, subsamples were treated according to the protocol published in Braig *et al.* (2013). Isotope ratios R are reported in the standard delta notation ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) in per mil (‰) relative to the international reference standard VPDB (carbon) and AIR (nitrogen) respectively, where

$$\delta_{\text{sample}} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000. \quad (5.1)$$

Additionally, diatom slides of selected stratigraphic horizons were prepared from not-homogenized subsamples of core EHW 7/08 following standard procedures (Braig *et al.* 2013), in order to calculate a diatom index DI (Hoffmann 1993, Schaumburg *et al.* 2005). The DI is a reference system for historic trophic levels and

water column TP concentrations (Table 5), which has been developed and calibrated on several Bavarian lakes. It is calculated from abundance and trophic preferences of the different taxa of benthic diatoms found in a stratigraphic core horizon, where

$$DI = \frac{\sum_{i=1}^n H_i \times G_i \times T_i}{\sum_{i=1}^n H_i \times G_i} \quad (5.2)$$

with H_i = relative abundance of taxon i , G_i = weighing factor for indicator quality of taxon i , T_i = trophic index of taxon i .

Table 5: Diatom index (Hofmann 1993) and ascribed trophic state vs. approx. TP corridors

Diatom index	trophic state	TP (OECD 1982)
1.00 – 1.99	oligotrophic	> 0.01 mg L ⁻¹
2.00 – 2.49	oligo - mesotrophic	
2.50 – 3.49	mesotrophic	0.01 – 0.035 mg L ⁻¹
3.50 – 3.99	meso – eutrophic	
4.00 – 5.00	eutrophic	0.035 – 0.1 mg L ⁻¹
Not defined	hypertrophic	> 0.1 mg L ⁻¹

Data on recent TP concentrations in Eishaussee was obtained from several other investigations (e.g. Melzer 1976, Raeder 1990, Sandmann and Beck, unpublished results).

All figures and statistical analyses were produced with the program OriginPro 8.6 (Originlab).

5.4 Results

5.4.1 Core description and XRF data

Both cores exhibit a relative high overall water content (EHW: 72.4 ± 6.1 % ; EHE: 69.9 ± 3.6 %) increasing from the bottom to the top of the core.

The core EHE 8/09 from the eastward, holomictic basin is rather homogenous and only weakly zoned in a lithological sense (Figure 16): While the bottom part (ca. 34 to 48.5 cm) consists of light-grey, fine grained mud of relatively low water content (67.5%), the central part (ca. 12.5 to 34 cm) is composed of brownish-grey mud

interrupted at several depths by barely visible, irregular pale laminae. The homogenous, brownish colored upper part is characterized by a rather rapid decrease in relative Ca content at 12.5 cm by 37.8%.

In core EHW 7/08 from the western meromictic basin, the lowermost, homogenous part (28 to 45 cm) consists of fine-grained mud and exhibits the lowest water (67.2 %) content of the entire core sequence, while the relative Ca concentration is highest here and rather uniform. Between the homogenous part and the continuously laminated upper zone, there is a short transition zone (25 – 28 cm) characterized by several, rather weak and irregular calcite laminae.

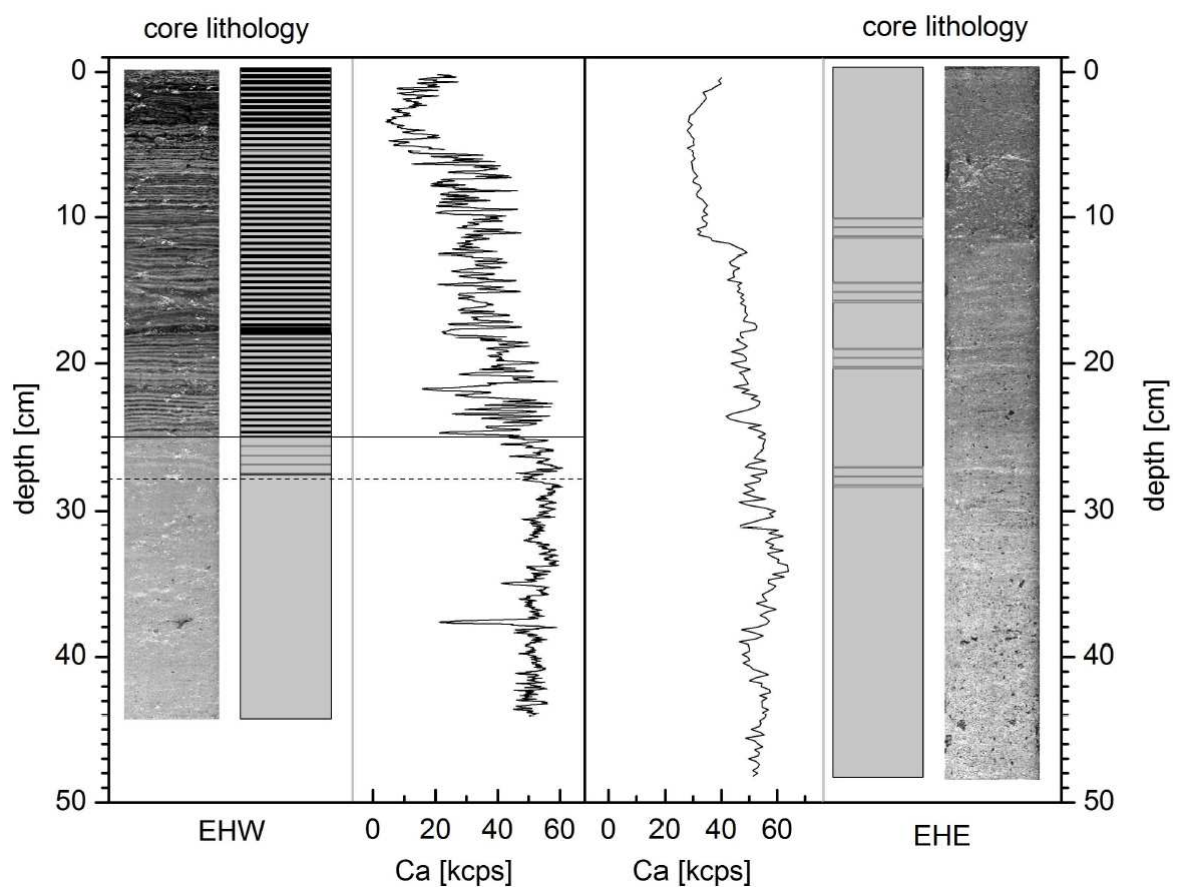


Figure 16: Photograph of half-core surfaces, core lithology and depth profiles of XRF-derived Ca counts (indicated as kilocounts per second) of cores EHW 7/08 (left) and EHE 8/09 (right). The dotted line marks the pre-laminated phase in the core of EHW, the solid line the onset of lamination.

A prominent feature of core EHW 7/08 is the continuous lamination of the sediment consisting of alternating light and dark layers in the upper part of the core (0 – 25 cm) (Figure 16). High-resolution Ca-scans (Figure 16) reveal a periodical oscillation of Ca contents where maxima always coincide with light layers, thus suggesting a linkage to seasonal calcite precipitation in the water column. The

general trend is an upward decline of Ca reversing only in the uppermost four centimeters.

5.4.2 Chronology

For cores EHW 7/08 and EHE 8/09, activity concentrations of ^{210}Pb and ^{137}Cs versus depth are shown in Figure 18 and Figure 19, the ^{210}Pb age models in figure 17.

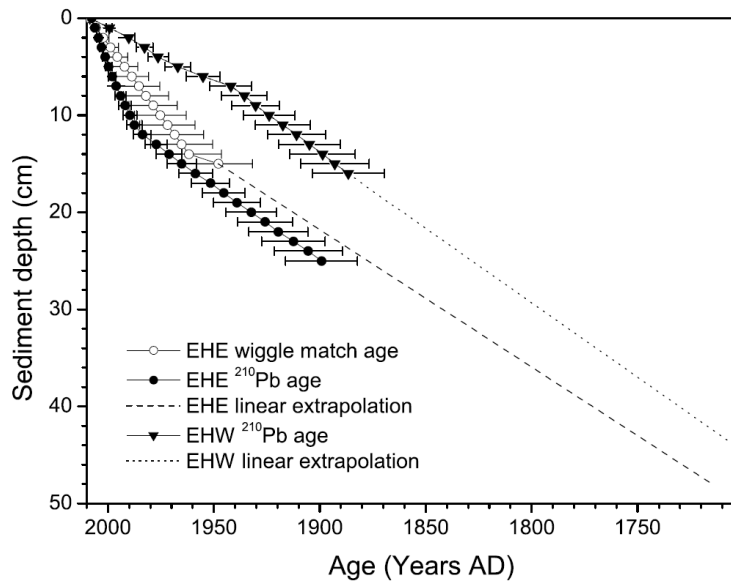


figure 17: Age-depth models for cores EHW 7/08 (circles) and EHE 8/09 (triangle). Filled symbols show the age-depth model derived from measurements of ^{210}Pb excess activity. Open circles show the wiggle match age model for EHE that was used for dating of this core. Dotted lines show the linear interpolation from the sedimentation rate obtained from the lowermost measurements.

Both cores exhibit a distinct upper peak of highest ^{137}Cs deposition (EHW: 1263 Bq kg^{-1} ; 2.5 cm / EHE: 146 Bq kg^{-1} ; 9.5 -11.5 cm), which can be attributed to the 1986 fallout produced by the Chernobyl nuclear accident and is in good agreement with the respective ^{210}Pb age-depth model (^{210}Pb age of ^{137}Cs maximum: EHW: AD $1986.4 \pm 3.3 \text{ y}$; EHE: $1986.6 \pm 3.8 \text{ y}$).

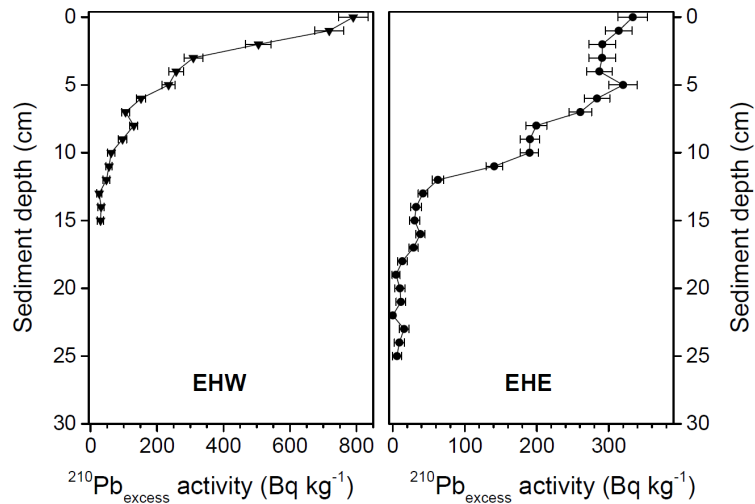


Figure 18: Depth distribution of $^{210}\text{Pb}_{\text{excess}}$ activity in EHW (left) and EHE (right). Error bars indicate two standard deviations.

As ^{210}Pb reaches background activity in 16 cm (EHW) and 26 cm (EHE) depth, core ages below this point had to be inferred from linear extrapolation of the sedimentation rates present in the lowest part of the ^{210}Pb profile.

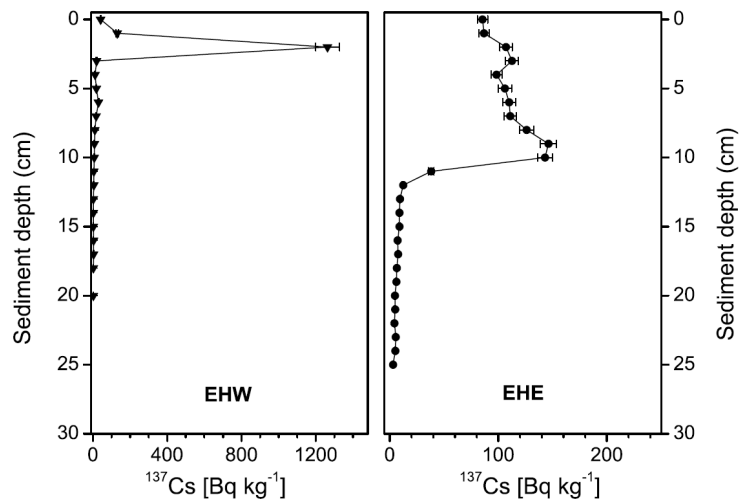


Figure 19: Depth distribution of ^{137}Cs activity in EHW (left) and EHE (right). Error bars indicate two standard deviations.

However, applying the age models based on the respective ^{210}Pb and ^{137}Cs data of EHW and EHE results in a moderate chronological mismatch (mean: $+13.3 \pm 6.9$ years), homogeneously visible between all respective signals of both cores with younger peak ages in EHE. This chronological offset is not constrained to $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, but is also visible between the proxies more directly associated with the effects of eutrophication (%TOC, %TN, TOC/TN). Thus, based on the assumption of a simultaneous impact of the biphasic eutrophication on both basins of Eishaussee, we decided to adapt the EHE age model to the ^{210}Pb age of EHW 7/08 within the error limitation of both models by peak-matching the $\delta^{13}\text{C}$ signals, as the latter show two

major signal changes (EHW: AD 1950 and 1820) clearly identifiable in both cores. We chose $\delta^{13}\text{C}_{\text{SOM}}$ in EHW and thus the respective ^{210}Pb and ^{137}Cs age model as a reference for peak matching, because the degree of conservation of the chronostratigraphic sequence is likely to be higher in the laminated sediments of the meromictic basin in which bioturbation was absent.

The applied age models result in total core ages of approx. 260 (EHE) and 300 (EHW) years. In EHW 7/08, the extrapolation of the age model dates the onset of lamination approximately to the year AD 1828.

5.4.3 Geochemistry, diatom index and water column TP data

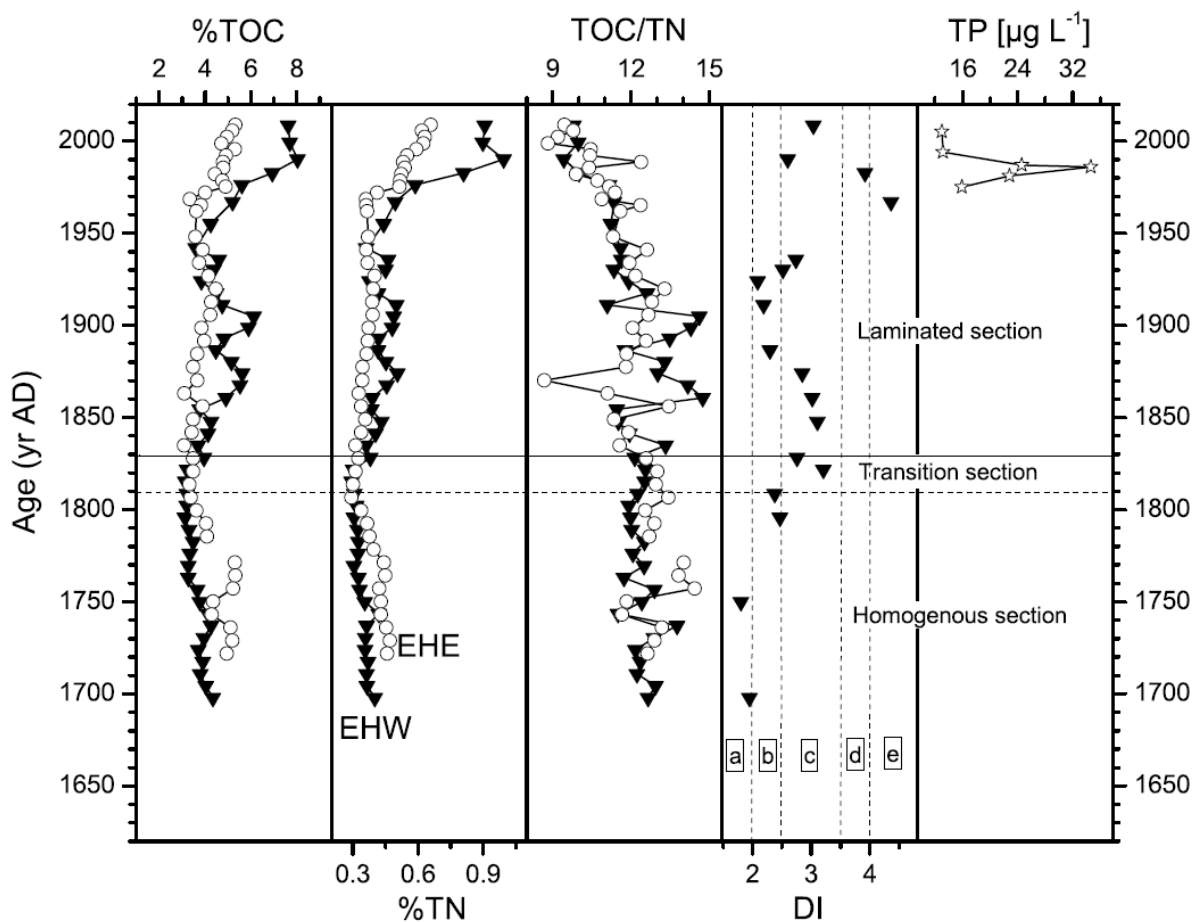


Figure 20: Water column (TP) and sediment core data (%TOC, %TN, TOC/TN, DI) for EHW 7/08 (filled triangle) and EHE 8/09 (open circles). In the DI graph, the following trophic ranges are separated by dashed lines: a. oligotrophic, b. oligo – mesotrophic, c. mesotrophic, d. meso – eutrophic, e. eutrophic

In Figure 20, sedimentary parameters of the cores from EHW 7/08 and EHE 8/09 as well as water column TP concentrations of EHW are plotted versus sediment age.

Before the onset of any lamination in the core from EHW (i.e. from AD 1698 to 1809), contents of TOC and TN show a minor, rather uniformly decline over time (TOC: 4.34% to 3.24%; TN: 0.40% to 0.30%). Similar trends, but slightly higher values, are observed in the core of EHE (TOC: 4.94% to 3.48%; TN: 0.46% to 0.30%). The mean differences between both basins (EHE-EHW) were 0.91% for TOC and 0.09% for TN. In the same stratigraphic level, TOC/TN values of both cores are oscillating around 12.5 and the DI exhibits the lowest values of the entire record (1.95 and 1.80), indicating an oligotrophic state of EHW during most of that period (Table 5). Towards the end of the pre-laminated phase there is a distinct increase in DI (from 1.80 to 2.38) indicating mesotrophic conditions in EHW around the start of lamination in AD 1828.

From the onset of lamination in the core from EHW on to the early 20th century, the contents of TOC and TN of both cores moderately increase (Figure 20). In this period TOC and TN values are higher in the core from EHW than in that from EHE (mean diff. EHW-EHE TOC: 1.14%; TN: 0.08%). In the core from EHE the TOC and TN increases (TOC: 3.48 to 4.47%; TN: 0.32 to 0.40%) are rather uniform and continuous until AD 1920. Thereafter both values slightly decrease until approx. AD 1970 (minimum TOC: 3.34; TN: 0.36%). In the core from EHW, there are several marked positive excursions concurrently visible in TOC and TN around AD 1828, 1848, 1874, 1905 and 1936. Until AD 1910, the TOC/TN ratio shows several distinct peaks in both cores but its mean still is between 12.4 (EHW) and 11.7 (EHE) and DI continually decreases to a low of 2.29 to 2.09 from AD 1887 to 1924, indicating an oligo-mesotrophic state of EHW at that time.

From AD 1930 on this trend reverses, when DI values steadily increase to a peak at 4.36 in AD 1967, revealing eutrophic conditions in EHW at that time. The trend to eutrophication is reflected by the development of TP in the water column of EHW, which shows a rapid increase from the earliest available value of 15.5 μgL^{-1} (AD 1975) to a distinct maximum with 34.6 μgL^{-1} in AD 1986. Marked TOC and TN increases in both cores occur during the second half of the 20th century as well. In the core from EHW, this trend starts in AD 1955 and peaks in AD 1990 with a more than twofold increase in each signal (TOC: 3.60 to 8.02%; TN: 0.36 to 0.99%). In the core from EHE, the rise of TOC and TN content starts somewhat later (1972) and continues to the upper end of the core sequence (TOC: 3.34 to 5.32%; N: 0.36 to 0.66%).

After AD 1986, both TP and DI values decline towards the upper end of the core sequences to values indicating recovery of the trophic situation in EHW towards a mesotrophic state. Similar declines of both TOC and TN contents in the core from EHW occur from 1990 on (TOC: 7.62%; TN: 0.91%). From AD 1924 to 2009, the TOC/TN content of both cores decreases continually to values of 9.9 (EHW) and 9.4 (EHE).

5.4.4 Stable isotope records

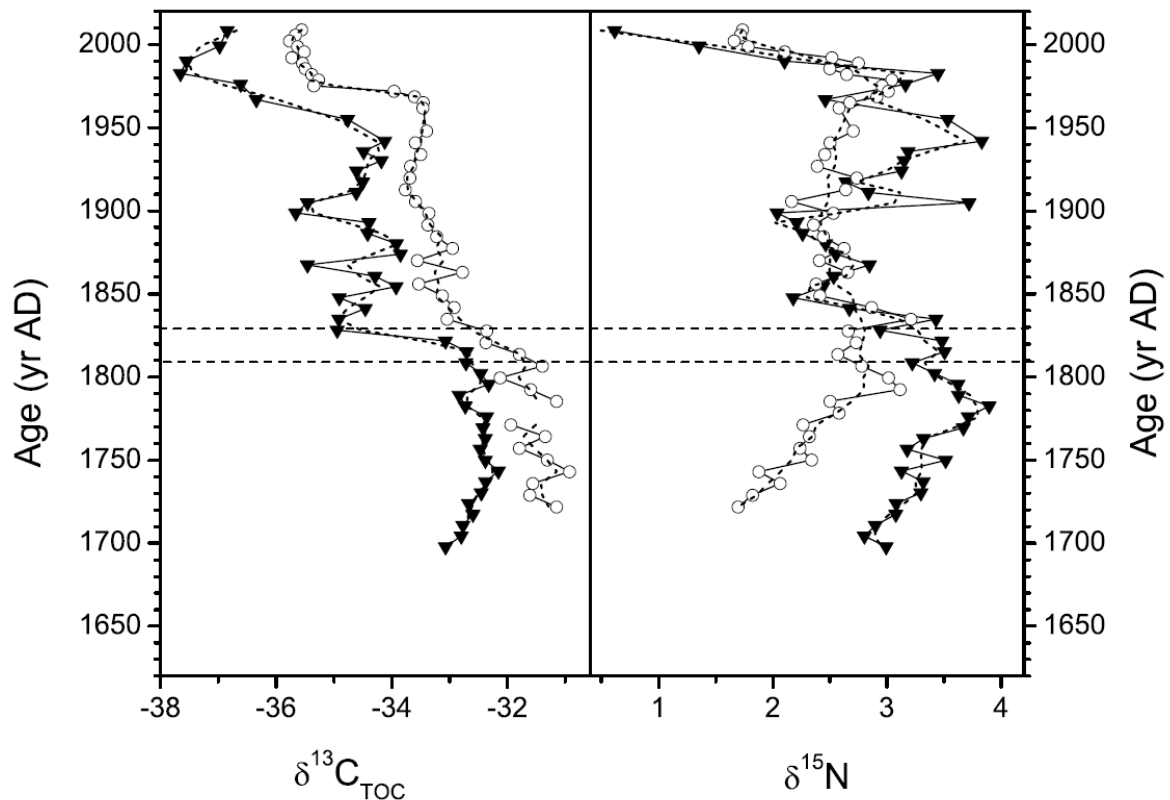


Figure 21: Stable isotope data ($\delta^{13}\text{C}_{\text{SOM}}$ and $\delta^{15}\text{N}$) of the sediment core EHW 7/08 (filled triangle) and EHE 8/09 (open circles).

Figure 21 depicts the $\delta^{13}\text{C}_{\text{SOM}}$ and $\delta^{15}\text{N}_{\text{SOM}}$ values of both cores and their 5-point running means versus sediment age. Before AD 1809, the approximate date in which the onset of lamination started in the EHW core, the $\delta^{13}\text{C}_{\text{SOM}}$ values of both cores exhibit a mean difference of 0.82‰ and are rather uniform, with more negative values in the core from EHW. The latter remains valid for the entire core sequences following thereafter. The respective $\delta^{15}\text{N}_{\text{SOM}}$ signals in this period have a mean offset of 0.77‰ with higher values in the core from EHW and show a distinct increase over time peaking at the end of the 18th century in both cores (EHE: 1.70 to 3.12‰; EHW: 2.99 to 3.90‰).

From then on to the onset of lamination in the core from EHW, both $\delta^{13}\text{C}_{\text{SOM}}$ and $\delta^{15}\text{N}_{\text{SOM}}$ signals decrease considerably ($\delta^{13}\text{C}_{\text{SOM}}$ EHE: -31.40 to -32.36‰; EHW: -32.32 to -34.94‰; $\delta^{15}\text{N}_{\text{SOM}}$ EHE: 2.99 to 2.66‰; EHW: 3.90 to 2.94‰) and the offset between both cores changes:

For the entire period from the onset of lamination in EHW until the middle of the 20th century, the mean difference between the respective $\delta^{13}\text{C}_{\text{SOM}}$ signals increases to 1.03‰. Both signals show a moderate decline to -35.67‰ (EHW) and -33.72‰ (EHE) around AD 1900, but increase slightly from then on until the middle of the 20th century (to -34.12‰; in EHW and -33.48‰ in EHE:). While the signal in the core from EHE is rather constant around a mean of -33.10‰ \pm 0.64, $\delta^{13}\text{C}_{\text{SOM}}$ in the core from EHW shows a higher variability around a mean of -34.35‰ \pm 0.79.

The offset between the $\delta^{15}\text{N}_{\text{SOM}}$ signatures of both cores decreases to a mean difference of 0.31 ‰ between the begin of lamination in the core from EHW and the end of the 19th century, while both signals exhibit an overall increasing trend.

From the begin of the 20th century to approx. 1986, this overall increase in $\delta^{15}\text{N}_{\text{SOM}}$ continues in both cores, but the signal in the core from EHW exhibits several distinct positive excursions (peak height: AD 1905: +1.38‰, 1942: +1.28‰, 1986: +0.89‰) and an overall larger variability, that are not equally present in the core from EHE.

From AD 1986 on, both $\delta^{15}\text{N}_{\text{SOM}}$ signatures show an expressed decrease, which continues to the upper end of the core sequence in EHW but not in EHE, where it stops in 2002.

As well, there is a considerable negative drop in the $\delta^{13}\text{C}_{\text{SOM}}$ signatures of both cores (EHW: -3.53‰ EHE: -2.25‰), which starts in the middle of the 20th century in EHW and somewhat later in EHE (AD 1968). In the core from EHW, this trend reverses towards the upper end of the core sequence after peaking in AD 1983.

5.5 Discussion

5.5.1 Meromixis and phases of eutrophication

As opposed to holomictic water bodies, meromictic lakes exhibit a bottom water layer (monimolimnion) permanently isolated from the periodically circulating upper waters (mixolimnion) by a vertically sharply defined zone characterized by a steep salinity increase (chemocline) (Findenegg 1937, Wetzel 2001). One of the several reasons for the formation of meromixis in a formerly holomictic lake is termed endogenic or biogenic (Hutchinson 1957, Wetzel 2001), as here the fundamental increase in salinity of bottom waters arises from sedimentary decomposition of accumulating autochthonous organic matter. On a seasonal basis, the formation of a chemocline can also be observed in holomictic lakes, but it is normally homogenized by semiannual overturns here. Nevertheless, this temporary salinity increase can be intensified during periods of elevated primary productivity induced by eutrophication processes. If such intensification is then accompanied by meteorological conditions of low wind-induced mixing, salinity can cumulate in the unperturbed water layers and increase the stability of bottom water stratification to a point where it cannot be destroyed even by stronger wind events (Jöhnk 2003, Boehrer and Schultze 2009, Braig *et al.* 2010).

Likewise, the meromixis present in the western basin of Eishaussee could have been induced by an early eutrophication, as is indicated by the increase in DI from AD 1800 on, which reveals an considerable trophic level rise present shortly before the onset of lamination in EHW around AD 1828. The weak, irregular laminae present in the core of EHW shortly before the onset of continuous lamination probably mark the transition period from holomictic to meromictic as has been reported from other lakes (Braig *et al.* 2013).

Once meromixis has established in a lake and the lower water layers are permanently stratified, the absence of both dissolved oxygen and significant turbation in bottom waters can have fundamental effects on the preservation of the sedimentation sequence: In an investigation of 300 Finnish lakes, Ojala *et al.* 2000 identified meromixis as a strong predictor for the presence of annually laminated sediments. Therefore, the onset of lamination in the sediment record of EHW in AD 1828 most likely marks the onset of stable meromictic conditions as induced by an earlier eutrophication.

Although DI data are not available for the eastern basin of Eishaussee, it seems reasonable to assume that EHE was affected in a similar manner by the eutrophication process because of the close proximity of the interconnected basins. The surface drainage originating from a small lake close to the rural estate of Staltach is a possible source of an early anthropogenic impact into EHE and EHW.

However, the essential factors for the conversion of temporarily increased bottom water stability into a permanent meromixis are the timing of and the depth to which wind-induced mixing reaches in a lake (Jöhnk 2003). As both basins of Eishaussee are likely to exhibit similar wind fetch, the difference in maximal depth might have been the reason why meromictic conditions could only establish in the deeper, westward basin EHW, but not in EHE.

While discharge from the growing and later abandoned rural estate of Staltach (deconstruction of the brewery in AD 1920, Bukovec and Exner 1994) is likely to have contributed to the the early eutrophication and trophic recovery following afterwards, the more recent increase in DI, TOC and TN content and TP clearly is in line with the general process of anthropogenic eutrophication of the Osterseen lake district starting around 1950 (Melzer 1976) and its specific impact on Eishaussee from 1970 (Raeder 1990, Braig *et al.* 2013). TOC and TN sedimentary concentrations in the core from EHW reflect the water column TP trend peaking in AD 1986 and declining afterwards in more detail than the respective parameters of EHE. This might be due to the fact that bulk OM conservation is more expressed under anoxic than under oxic sediment conditions (Lehmann *et al.* 2002), which probably has contributed to the consistently higher TOC and TN concentrations in the core from EHW from the onset of meromixis on as well. Moreover, bioturbation in the oxic basin apparently has smoothed geochemical signals in the EHE record. This effect was absent in the anoxic EHW basin explaining the larger scatter of the data after onset of lamination. The overall increase of sedimentary TOC/TN towards the bottom of both cores can be interpreted as a sign of active denitrification in deeper sediment layers (Sarazin *et al.* 1992) in both basins or attributed to higher OM fractions of vascular plant remains (aquatic macrophytes, terrestrial vegetation), while the absolut value present in upper sediment layers indicates a dominance of autochthonous OM, as algal OM is known to exhibit C/N signatures between 7 - 9 (Meyers and Teranes 2001).

5.5.2 Sedimentary $\delta^{13}\text{C}$

For decades, the carbon stable isotopic signature of SOM has been used as a reliable marker for eutrophication processes in limnic systems (e.g. Gu *et al.* 1996; Choudhary *et al.* 2009). When autochthonous primary production provides the principle source of SOM, productivity increases caused by anthropogenic eutrophication will be recorded as $\delta^{13}\text{C}_{\text{SOM}}$ increases, as the preferential uptake of the heavier carbon isotope by phytoplankton will deplete ^{13}C in the epilimnetic DIC pool, which in turn will be reflected in the biomass produced and deposited in the sediment thereafter (Farquhar *et al.* 1989, Meyers and Teranes 2001).

But eutrophication processes are often accompanied by anoxic conditions in the water column or sediment, as the elevated OM sedimentation creates a lasting depletion of oxygen in bottom waters (Brenner *et al.* 1999, Drew *et al.* 2008). This can give rise to anaerobic decomposition of the sedimented organic matter by microbially mediated carbon cycling processes such as sulphate reduction, denitrification, chemoautotrophy, methanogenesis and methanotrophy (Hollander and Smith 2001; Liikanen and Martikainen 2003).

Methanogenesis can be the principal (>95%) pathway of anaerobic remineralisation in lacustrine environments (Meyers and Ishiwatari 1993, Maerki *et al.* 2009). Both the formation of methane through OM degradation (methanogenesis) as well as subsequent aerobic or anaerobic methane oxidation (methanotrophy) are associated with pronounced kinetic isotopic fractionation effects (formation: $\epsilon = 49 - 95\text{‰}$; oxidation: $\epsilon = 4 - 30\text{‰}$, Whiticar 1999). Thus, compared to the substrate, both bacterial biomass and CO_2 originating from methane oxidation are considerably depleted in ^{13}C . Thus, ^{13}C depleted carbon sources can be reintegrated into the epilimnetic DIC pool. Via the assimilation of such ^{13}C depleted DIC into photoautotrophic biomass, methanogenesis and -trophly can be the dominating control of the isotopic composition of SOM. Hollander and Smith (2001) proposed a conceptual model for the response of sedimentary $\delta^{13}\text{C}_{\text{SOM}}$ on eutrophication processes. For a wide TP range (ca. 0.05 to 0.175 mg L^{-1}), they predicted a dominating influence of ^{13}C -depleted OM derived from microbial carbon cycling processes on the carbon isotopic signature of SOM. Only when TP is above or below the proposed TP range, the primary input signal of primary production will be the dominant control of $\delta^{13}\text{C}_{\text{SOM}}$.

Since then, several investigations proved the practical relevance of this conceptual model which predicts a determining influence of bacterially mediated carbon cycling processes such as methanogenesis and –trophly on $\delta^{13}\text{C}_{\text{SOM}}$ (e.g. Teranes and Bernasconi 2005, Woodward *et al.* 2012). However, as these processes are constrained to strictly anoxic compartments, their impact on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of SOM was thought to be controlled by the extent of stagnation and bottom water anoxis (Hollander and Smith 2001, Teranes and Bernasconi 2005). A case study from a lake adjacent to Eishaussee, Fischkaltersee, however, showed that methanogenesis was the dominant influence on $\delta^{13}\text{C}_{\text{SOM}}$ even in periods when bottom waters were permanently destratified and oxygenated for lake-restoration purposes (Braig *et al.* 2013). It is a common result of such countermeasures against the effects of anthropogenically induced eutrophication that, despite a successful oxigenation of bottom waters, the sediment remains unaffected and persists as anoxic compartment for microbial recycling processes (Gächter and Wehrli 1998, Teranes and Bernasconi 2000, Grochowska and Gawronska 2004).

Likewise, the widely synchronous development of the $\delta^{13}\text{C}_{\text{SOM}}$ profiles both in the core of the meromictic as well as the holomictic basin of Eishaussee is compliant with the model proposed by Hollander and Smith, as both signals are constantly too negative to be explained by varying input of photoautotrophic biomass alone, which typically exhibits $\delta^{13}\text{C}$ signatures of -28‰ (Meyers and Lallier-Verges, 1999). As well, the simultaneous reaction of $\delta^{13}\text{C}_{\text{SOM}}$ in both basins to each of the two consecutive increases in trophic level in Eishaussee is a considerable negative drop in signal, as is predicted by the named model within the present TP range. The reversal of the negative trend present in the uppermost samples of the cores of EHW as well as EHE likely reflects the decline of anthropogenic eutrophication in recent years as documented by the TP and DI records.

Thus, we conclude that the synchronicity of the $\delta^{13}\text{C}_{\text{SOM}}$ curves of the cores of EHW and EHE reflects not solely the signal of photoautotrophic primary production but rather the dominating influence of microbial recycling processes, such as methanogenis and subsequent methanotrophy, which have been intensified by a biphasic anthropogenic eutrophication. However $\delta^{13}\text{C}_{\text{SOM}}$ is not linearly correlated with epilimnetic primary productivity in Eishaussee as reflected by DI and TP. Such a delay has been observed already at adjacent Fischkaltersee by Braig *et al.* (2013)

and has to be considered when using $\delta^{13}\text{C}_{\text{SOM}}$ for the trophic history reconstruction of a lake.

However, in a meromictic basin with a stable chemocline and thus a defined oxic-anoxic boundary, several other carbon cycling processes such as deep oxygenic and anoxygenic photosynthesis, sulphate reduction and chemolithotrophy can be present and potentially have a significant impact on $\delta^{13}\text{C}$ of SOM:

When the chemocline is situated within the euphotic zone (where $\geq 1.5\%$ of surface irradiance is available, Wetzel 2001), extensive photosynthetic primary production is possible here as well. Camacho *et al.* (2001) found a photoautotrophic community consisting of various diatom species, thiophile Cryptophyceae (*Cryptomonas*) and phototrophic sulfur bacteria (*Amoebobacter cf. purpureus*) in the meromictic Lake Cadagno (Italy). They were able to show that up to 41% of the total carbon assimilation in the lake occurred at the chemocline, allowing for a possible effect of this OM on the carbon isotopic signature of SOM, as seston present in the chemocline exhibited $\delta^{13}\text{C}$ values of -36‰ to -39‰ contrary to values of -27‰ in the epilimnion.

Phototrophic sulfur bacteria are a common phenomenon in meromictic lakes and can provide up to 80 – 90% of the entire primary production here (Ivanov *et al.* 2001). When the oxic-anoxic interface, where oxygen and hydrogen sulphide from sulphate reduction can equally be present, is within the euphotic zone, H_2S is oxidised by phototrophic sulfur bacteria during anoxygenic photosynthesis, which can produce considerable amounts of ^{13}C depleted biomass (Zyakun *et al.* 2009).

While the presence of H_2S in the monimolimnion of EHW has been confirmed by all investigations, the long-term secchi disk range of 4 – 6 m indicates that a sufficient amount of light is not available at the chemocline at 14 m, as the Secchi readings roughly correspond to a euphotic depth of 10 – 12.2 m (Tilzer 1988).

But even when the chemocline is well below the photic zone, a substantial contribution of ^{13}C -depleted OM to SOM can be provided through dark carbon fixation by chemolithotrophic organisms (e.g. Casamayor *et al.* 2012). Hadas *et al.* (2009) found that in monomictic Lake Kinneret 20 – 25 % of the annual primary production was derived from chemolithotrophic sulphide oxidation, which was associated with $\delta^{13}\text{C}$ values of -39‰ .

Sulphate reduction is another microbially mediated carbon cycling process, which is common in meromictic basins (Matsuyama and Saijo 1971), as the permanent

stratification allows for bottom water accumulation of considerable amounts of SO_4^{2-} derived from aerobic OM degradation or the oxidation of H_2S (Schwörbel and Brendelberger 2005).

While the process of sulphate reduction can be closely coupled to anaerobic methane oxidation (Iversen and Blackburn 1981), methanogenesis is inhibited by sulphate concentrations above $100 - 150 \mu\text{g ml}^{-1}$ (Winfrey and Zeikus 1977). In EHW, measured concentrations of SO_4^{2-} range from $17 - 25 \mu\text{g mL}^{-1}$ (Melzer 1976) and are therefore too low for an inhibition effect, although these values have been detected in the upper water column. But it has been pointed out that relevant SO_4^{2-} concentrations are limited rather to bottom waters and the upper sediment zone, while methanogenesis can prevail in the deeper sulphate-free sediment layers (Winfrey and Zeikus 1979, Nauhaus 2003).

In summary, our results indicate that permanent anoxic conditions in the water column are not necessarily a prerequisite for a dominating influence of various microbially mediated secondary carbon cycling processes on $\delta^{13}\text{C}$ of settling OM, as the deeper layers of the sediment usually remain as an anoxic compartment.

However, there exists evidence partly from incubation experiments that the degree of oxygenation in the upper sediment zones can have contrary effects on the early diagenetic alteration of the carbon isotopic signal of the sedimented OM after burial:

Lehmann *et al.* (2002) compared the results of oxic and anoxic incubation experiments to sediment data from eutrophic Lake Lugano. Due to high OM sedimentation rates, oxygen penetration into the sediment is rather low there, which was concluded from the presence of well-preserved annual laminations. The anoxic incubation as well as sediment data concordantly reveal a depletion in the carbon isotopic signal when compared to the initial composition of settling OM ($\Delta\delta^{13}\text{C} -1.5\text{‰}$), while during oxic incubation, higher bulk mass loss and a decrease of $\delta^{13}\text{C}$ were found. They attributed this to differences in the selective preservation of isotopically light SOM.

For both basins of Eishaussee, no data is available on the original isotopic composition of recent particulate organic matter. Thus, it cannot be excluded that the observed offset between the $\delta^{13}\text{C}_{\text{SOM}}$ of both basins is mainly the result of differences in preburial water column processes. As discussed above, several other processes that are likely to be present in a meromictic basin can have a pronounced impact on the carbon isotopic composition of SOM by adding ^{13}C depleted biomass.

5.5.3 Sedimentary $\delta^{15}\text{N}$

Similar to the relation between $\delta^{13}\text{C}$ of OM and epilimnetic primary productivity in marine environments a robust correlation between the consumption of the surface water DIN pool (as a proxy for the intensity of photoautotrophic assimilation) and $\delta^{15}\text{N}$ of autotrophic biomass has been found (Altabet and Francois 1994). Although this relationship has been shown to be a relevant control of $\delta^{15}\text{N}_{\text{SOM}}$ in several lakes as well (e.g. Teranes and Bernasconi 2000, Braig *et al.* 2013), its general applicability for the reconstruction of the trophic history in lacustrine environments is often confined by the fact that here nitrogen is rather not the factor limiting the extent of primary production in most lake systems (Wetzel 2001). Thus, consumption of the surface water DIN pool might not be sufficient for a $\delta^{15}\text{N}$ effect to become visible in SOM.

As an additional similarity to $\delta^{13}\text{C}_{\text{SOM}}$, several other processes associated rather with the extent of anoxic microbial activity than with the intensity of primary productivity can have a significant impact on $\delta^{15}\text{N}_{\text{SOM}}$. Denitrification in the water column for example leaves the remaining DIN pool considerably enriched in ^{15}N , as here the formed dinitrogen depleted in ^{15}N is not recycled but permanently removed from the system via ebullition (Meyers and Teranes 2001). The strong associated ^{15}N discrimination can mask a potentially existing isotope effect caused by primary productivity. As the intensity of denitrification in a lake is greatly controlled by the extent of anoxia in the water column, increased OM sedimentation and the associated oxygen consumption in bottom waters as during phases of eutrophication can result in elevated $\delta^{15}\text{N}_{\text{SOM}}$ signatures (Teranes and Bernasconi 2000). Thus, in Eishaussee the observed increases in $\delta^{15}\text{N}_{\text{SOM}}$ present in both cores during the two phases of eutrophication could be a combined result of increased primary production and intensified denitrification.

However, there is no concordant rise in the TOC/TN of both cores from Eishaussee as might be expected because of the systemic N loss during extensive denitrification. As has been discussed above, the TOC/TN increase towards the bottom present in both cores rather indicates active denitrification in the sediment, which is not associated with the pronounced fractionation factors of water column denitrification (Brandes and Devol 1997). Additionally, while in theory the difference in $\delta^{15}\text{N}_{\text{SOM}}$ between both basins should be more expressed during the meromictic phase than before, the considerable offset between both signals present in the pre-

laminated core section vanishes after the onset of meromixis in EHW almost entirely. As well, especially in the core from EHW $\delta^{15}\text{N}_{\text{SOM}}$ is highly variable during the meromictic phase, when both bottom water anoxia and trophic level were relatively constant. In addition, the signals of both cores exhibit a strong and concordant positive drift before the onset of lamination and can therefore not be related to the biphasic anthropogenic eutrophication or the meromixis in EHW. But the rather complex lacustrine N cycle (Meyers and Teranes 2001) holds several other processes not directly related to the trophic status that potentially could have influenced $\delta^{15}\text{N}_{\text{SOM}}$ in Eishaussee. As land-based denitrification allows for considerable ^{15}N enrichment (+5 to +20‰; Talbot 2001), inflow of manure from the Staltach estate as well as later on inflow of human sewage from the camping site could as well have contributed to the peaks $\delta^{15}\text{N}_{\text{SOM}}$ present in both cores during the two phases of eutrophication.

The rather high variability of the N isotopic signal in the core from EHW after the onset of meromictic conditions could indicate varying input of bacterial biomass, as the latter typically is rather depleted in $\delta^{15}\text{N}$ (Lehmann 2002) and large multi-year-shifts in abundance between different species have been reported for the bacterial community at the chemocline in meromictic basins (Tonolla *et al.* 2005). On the other hand, the absence of bioturbation in EHW after the onset of meromixis might as well be a possible explanation for the higher degree of conservation in this part of the core sequence.

Since $\delta^{15}\text{N}_{\text{SOM}}$ has often been used as an additional proxy for trophic history reconstruction of lacustrine systems, it has been controversially discussed whether the input $\delta^{15}\text{N}$ signal of sedimented OM is significantly changed by post-burial diagenetic processes.

While several investigations reported no (Hodell and Schelske 1998, Teranes and Bernasconi 2000) or minor (Gälmann *et al.* 2009) alterations of $\delta^{15}\text{N}$ in OM after sedimentation, Lehmann *et al.* (2002) found a $\delta^{15}\text{N}$ depletion of 1.2‰ in recently sedimented biomass vs sediment trap material in the eutrophic lake Lugano. As the effect of oxic vs anoxic sediment conditions on early diagenesis was investigated in a series of incubation experiments, the difference between both sediment regimes is of particular interest for the interpretation of the results of our investigation: During anoxic sediment incubation, $\delta^{15}\text{N}$ decreased by 3‰, which was attributed to the addition of heterotrophic biomass depleted in ^{15}N , while in the oxic incubation, the

$\delta^{15}\text{N}$ of OM returned to its initial value after a 3‰ increase. Differences in the kind and intensity of the present microbial activity as controlled by the availability of oxygen were discussed as the most likely cause for the observed differences in $\delta^{15}\text{N}$ between the oxic and the anoxic incubation experiments.

The ^{15}N depletion observed under anoxic conditions might as well represent a possible explanation for the drifts to more negative $\delta^{15}\text{N}_{\text{SOM}}$ values concordantly present in the cores after the onset of both eutrophication periods in Eishaussee, as it is reasonable to assume that each of the two phases was associated with elevated OM sedimentation and thus, a relative intensification of sediment anoxia in both basins.

As for $\delta^{13}\text{C}_{\text{SOM}}$, no input signal is available for $\delta^{15}\text{N}$ in both basins of Eishaussee, so it cannot be excluded that especially the offset in signal between both basins before the onset of meromictic conditions in EHW is due to differences in water column processes. However, as the first eutrophication episode resulted in meromictic conditions in the deeper basin, the relative increase in sediment anoxia was probably more expressed in EHW than in EHE and elevated post-burial addition of bacterial OM depleted in ^{15}N might have resulted in the observed greater decline in $\delta^{15}\text{N}_{\text{SOM}}$ in EHW.

5.6 Conclusions

Carbon and nitrogen isotopic signatures of sedimented lacustrine organic matter have been used widely to infer information on water column processes, particularly on the history of eutrophication of a given lake. Although the underlying relationship between the extent of epilimnetic primary production and the isotopic signature of the produced organic matter is well understood and has been proven to be of relevance for SOM in many lacustrine systems, pivotal investigations revealed that the primary signal of photoautotrophic production in the upper water layers can as well be masked by secondary recycling processes such as the strictly anoxic processes of methanogenesis and denitrification. As an additional limitation, there exists evidence on opposed effects of postburial diagenetic processes on $\delta^{13}\text{C}_{\text{SOM}}$ and $\delta^{15}\text{N}_{\text{SOM}}$ depending on the degree of sediment oxygenation, so that, in theory, a similar primary productivity input signal could be differentially preserved in SOM of lakes which show different mixis types.

The circumstance that Eishaussee consists of two separate basins, which exhibit contrasting limnological properties in terms of their mictic situation and thus, bottom water oxygenation, render the lake an ideal study object for a comparative investigation on the impact of eutrophication on the carbon and nitrogen stable isotopic signal of SOM as well as its conservation under contrasting conditions of bottom water oxygenation.

The results of our investigation reveal that especially in situations of anthropogenic eutrophication, sedimentary trends of $\delta^{13}\text{C}_{\text{SOM}}$ and $\delta^{15}\text{N}_{\text{SOM}}$ will not always reliably reflect the intensity of autochthonous primary productivity, but rather the dominating effect of increasing bottom water anoxia and associated microbial reworking processes such as methanogenesis and denitrification. For $\delta^{13}\text{C}_{\text{SOM}}$, the results obtained for both basins of Eishaussee provide additional evidence for the practical relevance of the conceptual model proposed by Hollander and Smith (2002). As is predicted by this model within the TP range valid for the Eishaussee record, the reaction of $\delta^{13}\text{C}_{\text{SOM}}$ in the meromictic as well as the holomictic basin to the biphasic impact of anthropogenic eutrophication is a negative drop in the otherwise relatively constant signal. Although it is an important limitation for the use of $\delta^{13}\text{C}_{\text{SOM}}$ in the reconstruction of historic eutrophication processes that this reaction is not related in a linear way to the trophic state as obtained from the DI and TP, it is encouraging for

a sustained use of $\delta^{13}\text{C}_{\text{SOM}}$ in studies of historic eutrophication that the qualitative reaction of the signal to subsequent trophic level increases is comparable in a holomictic as well as a meromictic basin.

A similar conclusion for the use of $\delta^{15}\text{N}_{\text{SOM}}$ for trophic history reconstruction in lacustrine environments is not supported by the results of our investigation, as in Eishaussee this signal is highly variable over both core records and exhibits no consistent reaction to the biphasic eutrophication process. This might be due to the fact that in the more complex limnic N cycle many processes exist that can significantly influence $\delta^{15}\text{N}_{\text{SOM}}$ which are rather associated with the extent of anoxia than with epilimnic primary productivity.

5.7 Acknowledgements

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6 General Discussion and Conclusions

6.1 Applicability of the oxygen stable isotope signal $\delta^{18}\text{O}$ for tracing limnological key processes

In lacustrine environments, the most common application of the signal $\delta^{18}\text{O}$ induced by evaporative stable isotope enrichment is as a proxy in water mass balance investigations (Dinçer 1968; Gat and Bowser 1991, Blasch and Bryson 2007, Mayr et al. 2007, Yi et al. 2008). As introduced above, the isotope mass balance approach allows both for an estimation of the evaporation to inflow ratio of a lake (under the precondition of hydrologic steady state) as well as to trace lake-to-lake changes in the situation of a coupled evaporative system (Dinçer 1968). The latter is in particular applicable in the case of a chain of sequentially throughflown lakes (Gat and Bowser 1991), where the outflow of the previous lake provides the inflow to the lake following downstream.

In the case of the Osterseen lake district, water retention time as well as the exact flow pattern in the interconnection of the individual lakes are unquestionably limnologic research topics which, although of considerable interest, have not yet been sufficiently addressed. As other parameters such as h , δA , δl or bathymetric data for the individual basins could be interpolated or obtained from other sources (e.g. the GNIP network), an isotope mass balance investigation of the Osterseen lake district in theory would only require depth-profile water samples (for $\delta^{18}\text{O}$ and δD) collected in the individual lakes over a sufficient time interval (Gibson et al. 2002). This approach is a prerequisite specific to all isotope mass balance investigations conducted on stratified lakes in temperate climate zones. As with expressed seasonality there will be periods relatively free of evaporation (i.e. periods of ice cover), isotopic steady state δ^* will most likely not be reached, but can be estimated by a best-fit approach of the collected time-series of δL during the evaporative season (Gibson et al. 2002). As well, as the evaporative signal is generated only on the very water surface, it is important to account for the entire water column, because sampling during the stratified period would lead to an overestimation of the evaporative fractionation (and all parameters calculated therefrom), when conducted only on the water surface, as well as to an underestimation, when conducted below the mictic zone of the epilimnion. In the case of water layering, the equilibrium value

δ_L representing the respective mean of the net evaporation fractionation and the signal of the inflow will be visible only during overturn phases, when all water layers and their respective signature are completely uniform (Stichler et al. 2008).

The data collected during this thesis indicate that this approach cannot be easily applied to the complex hydrology of the Osterseen lake district. Despite preliminary investigations revealing that the equilibrium values collected in all lakes during the overturn phase are located on the same LEL with an elevation of 4.8 when plotted in $\delta^{18}\text{O}$ vs δD space and intersect the local MWL at the signature of local groundwater wells,

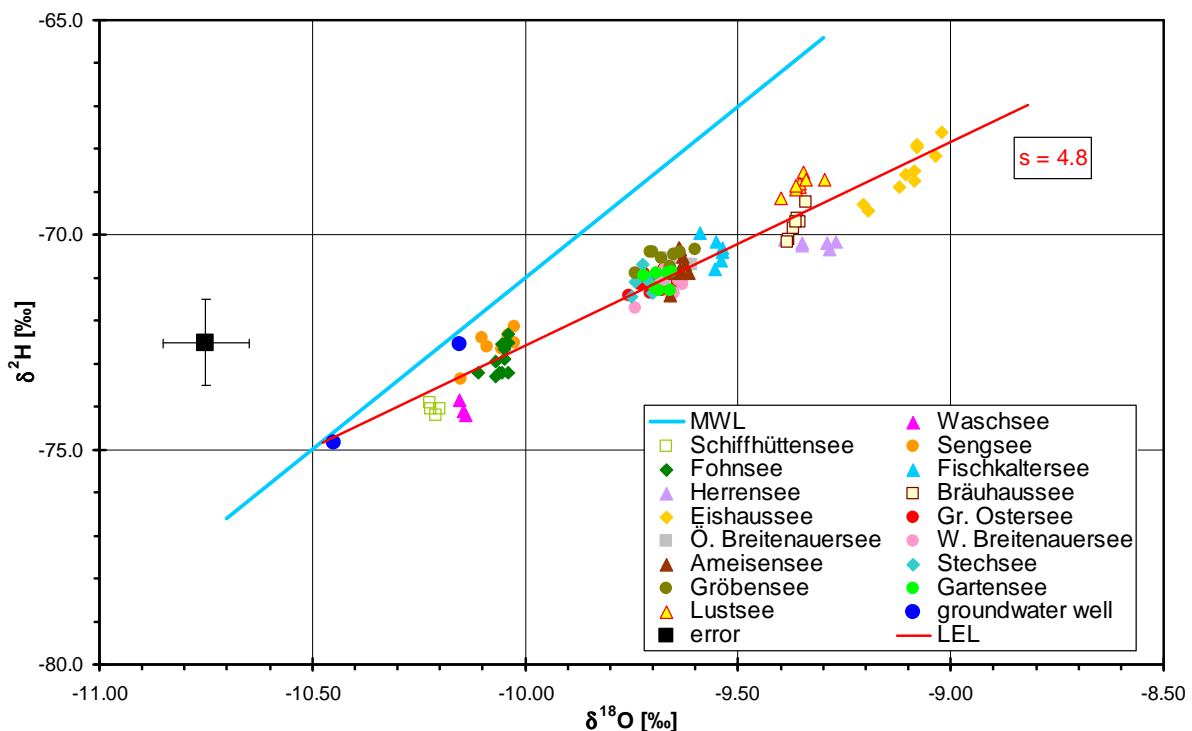


Figure 22: The meteoric water line (MWL, derived from data from the global network of isotopes in precipitation GNIP) valid for the Osterseen lake district and the LEL with an elevation = 4.8 as best-fit line of the $\delta^{18}\text{O}$ values measured in the lakes of the Osterseen lake district during annual overturn. Modified from Fuentes and Stichler, unpublished results.

the absolute signal differences in δ_L between the individual lakes and local groundwater as well as in the individual lakes during the evaporative period are only minor, thus allowing for a potentially large error when used in equations to determine admixing. In addition, a general limitation of the application of the chain-of-lakes effect in the tracing of lake-to-lake variations seems to be of considerable importance in the case of the Osterseen lake district, as the individual basins are stratified during most of the year. Thus, inflow or outflow will occur only to or from defined depth horizons, resulting in short-circuiting of the relevant lake volume and thus the effect of

evaporative fractionation. In that case, δ_L of the respective lake will not be a reliable indicator of its water balance (Dinçer 1968).

However, the sampling of both $\delta^{18}\text{O}$ and δD values conducted on Waschsee, Fohnsee and Eishaussee over almost one seasonal cycle reveals that in particular the signal of $\delta^{18}\text{O}$ is an ideal tracing method for limnologic key processes which is easily integrated into routine water sampling. One of the main advantages of the $\delta^{18}\text{O}$ method over other approaches such as water temperature measurements is that the isotope signal of a particular water layer changes only in the case of significant mass transport (Dinçer 1968). Thus, while even a pronounced drop in water temperature during the stratified phase as due to a cooling event is only the precondition for mixing to occur, a change in $\delta^{18}\text{O}$ in water layers formerly constant in signal reveals definitively significant convection of water masses. This was clearly visible in the reaction of $\delta^{18}\text{O}$ to limnologic phenomena in the investigated lakes: The polymixis of Waschsee was more obvious from the uniform $\delta^{18}\text{O}$ signal than from the respective temperature depth profile, as the latter indicated layering (presumably of diurnal character) on several occasions. In the meromitic Eishaussee, the permanent isolation of the monimolimnion was also reflected by $\delta^{18}\text{O}$ values significantly different from the mixolimnion over the whole period under investigation, while groundwater inflow into the hypolimnion of Fohnsee could be proven by a significant trend towards more depleted $\delta^{18}\text{O}$ values during the stratified season.

For applications where information on entrainment is needed, the investigation of $\delta^{18}\text{O}$ might be a relevant option, although it has to be stated that a locally defined entrainment event might remain undetected by depth profile sampling at a singular point in a larger lake. As expected, $\delta^{18}\text{O}$ and δD showed identical reactions to the observed limnological phenomena. In isotope water balance investigations, δD data are often used only as a measure for uncertainty, as separate estimates based on each of the tracers commonly have a maximum deviation of $\pm 10\%$ (Gibson et al. 2002). As sample preparation is more complex for the measurement of the $^2\text{H}/^1\text{H}$ ratio, the interpretation of the available δD data is beyond the scope of this investigation targeting an feasible approach easily integrated into routine sampling. Additionally, the range of $\delta^{18}\text{O}$ in epilimnetic waters during the evaporative enrichment observed during the period under investigation underlines an important implication for paleolimnologic studies reconstructing historic $\delta^{18}\text{O}$ or δD of lake water (and ultimately, from precipitation) from authigenic sedimental proxies such as

diatom frustules (Leng and Barker 2006), cellulose (Wolfe et al. 2007) chironomid head capsules (Wooller et al. 2004) or authigenic carbonates (Hayes et al. 1999). As a relevant temporal as well as vertical inhomogeneity in $\delta^{18}\text{O}$ of lake water has to be expected in lakes situated in zones with expressed seasonality, the spatiotemporal pattern of isotope exchange of the proxy with the ambient water has to be well known in order to be able to recognize a seasonal or spatial bias resulting from in-lake evaporative enrichment.

6.2 Impact of anthropogenic eutrophication on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM in Fischkaltersee and Eishaussee and influence of anaerobic pre- and postdepositional diagenetic processes

On the one hand, the most recent phase of anthropogenic eutrophication in the Osterseen lake district (ca. 1970 – 1990) has been the subject of limnologic research for decades (*cf.* Melzer 1976, Raeder 1990) and is documented for some lakes in detail (e.g. Steinberg and Fischer 1982). On the other hand, the earliest published historical investigations from before that phase (Apian in Bukovec and Exner 1994, Zorell 1941), which encountered the lakes in a state unaffected by the anthropogenic impact from 1970 on, give no qualitative or quantitative information on the original trophic status of the individual lakes. Therefore, sediment proxy data from Eishaussee obtained during this thesis allows the first insight into the preceding trophic history of the lake. As well, it reveals an earlier phase of presumably anthropogenic eutrophication affecting the Osterseen around 1828. Although because of catchment morphology it can be assumed that the impact of this early sewage inflow was constrained to Eishaussee and other lakes of the Staltach side chain, no data is available for the other lakes during this phase. But the oligotrophic state of Eishaussee indicated by the sedimental diatom index before that first eutrophication period is likely to represent the original, pre-human trophic status of the entire Osterseen lake district at that time, as has been reported from other carbonate lakes in comparable settings (Alefs 1997, Hoffmann and Schaumburg 2002, Mayr et al. 2010). Since the brewery was deconstructed in 1920 and the rural estate of Staltach subsequently abandoned, the impact of the pollution lifted and the sedimental DI indicates recovery to almost the initial state of the lake. Because of the latter fact, this early eutrophication episode might have remained undetected, despite its lasting impact on sedimentary isotope signals of Eishaussee. In particular the carbon isotope signal of SOM was affected in a substantial manner, but in a way contrary to the reaction predicted by classical theories for a trophic level increase.

As introduced in detail above, the classical model on the reaction of $\delta^{13}\text{C}_{\text{SOM}}$ on eutrophication predicts that phytoplankton OM enriched in ^{13}C , which results from the increasing depletion of ^{13}C in the surface water DIC pool observable during periods of intensified primary production, will provide the dominant control on $\delta^{13}\text{C}$ of SOM.

Therefore, stratigraphic increases in $\delta^{13}\text{C}_{\text{SOM}}$ have widely and consistently been interpreted as proxies of historic trophic level rises.

However, there also exist some published data of lacustrine systems where variations in $\delta^{13}\text{C}$ of SOM could not be brought in concordance with the respective eutrophication history when applying the classical model: In an investigation of 83 Florida lakes (Gu et al. 1996), a good positive correlation ($r = 0.82$, $p = 0.002$) between $\delta^{13}\text{C}$ of phytoplankton and Chl *a* (as a measure of the intensity of photoautotrophic production) was found for the upper water column, but for the same lakes, the correlation between Chl *a* and $\delta^{13}\text{C}_{\text{SOM}}$ was rather weak ($r = 0.61$, $p = 0.0001$). The investigators ascribed this to input of nonplanctonic OM of terrestrial origin, which was proposed to represent an important influence on $\delta^{13}\text{C}_{\text{SOM}}$ in oligotrophic to eutrophic basins, but not in hypereutrophic lakes, where the signal of photoautotrophic biomass was deemed to dominate. In another investigation, negative stratigraphic trends in $\delta^{13}\text{C}_{\text{SOM}}$ during documented eutrophication periods were explained as a possible result of ^{13}C -depleted sewage input and commented as “seemingly contradicting” to other sedimental trophic level proxies (Rosenmeier et al. 2004). More recently, similar negative trends have been linked to an impact of microbial OM as a result of increasingly anoxic conditions in the water column (e.g. Torres et al. 2012).

A broad variety of autotrophic and heterotrophic processes in the lacustrine C cycle are known to produce OM significantly depleted in ^{13}C , such as deep photosynthesis at the chemocline (Camacho et al. 2001), phototrophic sulfur bacteria (Ivanov et al. 2001, Zyakun et al. 2009) and dark fixation (Hadas et al. 2009). But in particular the combined effect of methanogenesis and subsequent methanotrophy bears the potential for a systematic and dominant impact on $\delta^{13}\text{C}_{\text{SOM}}$, because lacustrine eutrophication is often accompanied by elevated OM sedimentation rates as well as stagnant, suboxic bottom waters quite favorable for an intensification of methanogenic degradation processes. As well, both the bacterial biomass as well as the methane produced during the degradation of sedimented OM are considerably depleted in ^{13}C (formation: $\epsilon = 49 - 95\text{‰}$). As the methane diffusing upwards in the oxic zones of the water column can be reintegrated by methanotrophs into the epilimnetic DIC pool, the associated negative signature (oxidation: $\epsilon = 4 - 30\text{‰}$, Whiticar 1999) can become superimposed on the original $\delta^{13}\text{C}$ composition of DIC and overrule a potentially existent primary productivity signal. Only if the intensity of

primary productivity (and thus, OM sedimentation and burial rates) reaches extreme levels, there will be some kind of mass effect, according to the conceptual model established by Hollander and Smith (2001): They established a corridor of water column TP concentrations (werte), above and below which the signal of photoautosynthetic processes will dominate $\delta^{13}\text{C}_{\text{SOM}}$ again. The stratigraphic signals of $\delta^{13}\text{C}_{\text{SOM}}$ in Fischkaltersee and Eishaussee obtained during this thesis provide conclusive practical evidence for this conceptual model. However, because methanogenesis is a strictly anoxic process, another important control on whether methanogenesis can become the dominant control on $\delta^{13}\text{C}_{\text{SOM}}$ is often ascribed to a sufficient degree of water column anoxia (lit.). The investigation of $\delta^{13}\text{C}_{\text{SOM}}$ in the artificially aerated Fischkaltersee reveals that this is not necessarily a prerequisite, as an anoxic sediment is a common phenomenon even during long time aeration (Gächter and Wehrli 1998, Teranes and Bernasconi 2000, Grochowska and Gawronska 2004). Under such circumstances, the sediment provides an anaerobic compartment for the sustained production of methane, which then can become rapidly oxidized in the turbulent oxic water layers and subsequently integrated into the DIC pool.

Both the trends as well as the absolute values of $\delta^{13}\text{C}_{\text{SOM}}$ in both basins of Eishaussee reveal that here as well the intensity of epilimnic primary productivity is not likely to represent the dominating control. Together with the trophic history as reconstructed from sedimental (N and C content, diatom index) as well as water column (TP concentrations) markers, the stratigraphic C isotope variations in the sediment of both basins of Eishaussee are more compliant with the model proposed by Hollander and Smith than with the classical theory. Thus, the data obtained during the investigation of Eishaussee provide additional evidence for the relevance of this conceptual model as well as for the relative independency of the influence of methanogenesis/methanotrophy from water column oxygenation conditions.

$\delta^{15}\text{N}$ of SOM has been used by many investigations of lacustrine eutrophication as a proxy complementary to $\delta^{13}\text{C}_{\text{SOM}}$. The latter was deemed to be more reliable, as N limitation of primary production is the exception rather than the rule in limnic environments. Thus, the preferred consumption of ^{12}N by phytoplankton is not likely to be a relevant control of $\delta^{15}\text{N}$ of DIN here. However, the results of Fischkaltersee reveal that $\delta^{15}\text{N}_{\text{SOM}}$ can correlate more closely with the trophic evolution of a lake as

indicated by direct water column proxies than $\delta^{13}\text{C}_{\text{SOM}}$, which is dominated by the signal of methanogenesis.

But lacustrine N cycling is rather complex and in particular anoxic microbial processes not associated with the extent of surface water photoassimilation can have a significant impact. For the setting of Fischkaltersee and in particular Eishaussee with anthropogenic eutrophication affecting partly anoxic basins these processes include for example denitrification (*cf.* Meyers and Teranes 2001), input of bacterial biomass depleted in ^{15}N (Lehmann 2002, Tonolla 2005) or inflow of land-based sewage (e.g. Talbot 2001). Therefore, the observed stratigraphic variations of $\delta^{15}\text{N}_{\text{SOM}}$ in both basins of Eishaussee are likely to represent the combined impact of water column processes as well as possible postburial diagenetic alteration.

Another potential influence of considerable importance to reconstructions of historic water column processes using $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM is postburial diagenesis modifying the C and N isotope composition of SOM. However, there exists only conflicting evidence on their potential impact. Incubation experiments identified the degree of water column and sediment anoxia as a possible control of the quality of postburial isotopic alteration (Lehmann 2004), but in lacustrine environments, a quantitative and qualitative assessment of this effect and an identification of the controlling factors is difficult. The unique setting of Eishaussee of a singular lake with both an oxic and an long-time anoxic basin offers the possibility to explore the preservation of the water column input signals in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SOM under different oxygenation conditions.

7 References

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8 Appendix

Veröffentlichungen und Tagungsbeiträge

akzeptierte bzw. eingereichte Veröffentlichungen in Peer reviewed Journals

1. Entrainment, annual circulation and groundwater inflow in a chain of lakes as inferred by stable ^{18}O isotopic signatures in the water column

Emanuel Braig, Gerhard Welzl, Willibald Stichler, Uta Raeder and Arnulf Melzer

Journal of Limnology, 2010; 00(0): 278-286

2. Separating soil respiration components with stable isotopes: natural abundance and labelling approaches.

Emanuel Braig and Boris Tupek

iForest-Biogeosciences and Forestry 3: 92-94.

3. Fifty years of eutrophication and lake restoration reflected in sedimentary carbon and nitrogen isotopes of a small, hardwater lake (South Germany)

Emanuel Braig, Christoph Mayr, Gerald Kirchner, Andrea Hofmann, Uta Raeder and Arnulf Melzer

Journal of Limnology, 2013; 72(2): 262-279

4. Impact of anthropogenic eutrophication on sedimentary carbon and nitrogen isotope records from a meromictic and a holomictic basin of Lake Eishaussee (S-Germany)

Emanuel Braig, Christoph Mayr, Gerald Kirchner, Uta Raeder and Arnulf Melzer

submitted to Journal of Limnology

Tagungsbeiträge

1. Untersuchung der Hydrologie einer Seenkette anhand stabiler Isotope ($\delta^{18}\text{O}$)

Emanuel Braig, Uta Raeder & Arnulf Melzer

Deutsche Gesellschaft für Limnologie (DGL) Jahrestagung 2009 (Oldenburg),

2. Untersuchung der trophischen Vergangenheit des Fischkaltersees anhand von Sedimentproxies ($\delta^{13}\text{C}$ / $\delta^{15}\text{N}$).

Emanuel Braig, Uta Raeder & Arnulf Melzer

Deutsche Gesellschaft für Limnologie (DGL) Jahrestagung 2010 (Bayreuth)

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Braig E, Mayr C, Kirchner G, Hofmann A, Raeder U and Melzer A. 2013. Fifty years of eutrophication and lake restoration reflected in sedimentary carbon and nitrogen isotopes of a small, hardwater lake (south Germany). *Journal of Limnology* 72: 262-279.

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